U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-286 659

Guidelines for Preparing Environmental Test Plans for Coal Gasification Plants

Radian Corp, Austin, TX

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, NC

Jul 78

United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

EPA-600/7-78-134
July 1978

PB 286 659

Guidelines for Preparing Environmental Test Plans for Coal Gasification Plants

Interagency Energy/Environment R&D Program Report

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

187

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the INTERAGENCY ENERGY-ENVIRONMENT RESEARCH AND DEVELOPMENT series. Reports in this series result from the effort funded under the 17-agency Federal Energy/Environment Research and Development Program. These studies relate to EPA's mission to protect the public health and welfare from adverse effects of pollutants associated with energy systems. The goal of the Program is to assure the rapid development of domestic energy supplies in an environmentally-compatible manner by providing the necessary environmental data and control technology. Investigations include analyses of the transport of energy-related pollutants and their health and ecological effects; assessments of, and development of, control technologies for energy systems; and integrated assessments of a wide-range of energy-related environmental issues.

EPA REVIEW NOTICE

This report has been reviewed by the participating Federal Agencies, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Government, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/7-78-134

2.

3.
PB286659

4. TITLE AND SUBTITLE
Guidelines for Preparing Environmental Test Plans for Coal Gasification Plants

5. REPORT DATE
July 1978

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
G.C. Page, W.E. Corbett, and W.C. Thomas

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Radian Corporation
8500 Shoal Creek Boulevard
Austin, Texas 78766

10. PROGRAM ELEMENT NO.
EHE623A

11. CONTRACT/GRANT NO.
68-02-2147, Exhibit A

12. SPONSORING AGENCY NAME AND ADDRESS
EPA, Office of Research and Development
Industrial Environmental Research Laboratory
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED
Task Final; 5/76-12/77

14. SPONSORING AGENCY CODE
EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is William J. Rhodes, Mail Drop 61. 919/541-2851.

16. ABSTRACT
The report outlines a philosophy and strategy for preparing environmental assessment sampling and analysis (test) plans. Five major points of test plan development are addressed: (1) defining the test objectives, (2) performing an engineering analysis of the test site, (3) developing a sampling strategy, (4) selecting analytical methods, and (5) defining data management procedures. The important considerations involved in each area are discussed in relation to three types of environmental tests: (1) waste stream (Levels 1, 2, and 3), (2) control equipment, and (3) process stream characterization. Specific sampling and analytical methods are presented, with numerous references cited for more detailed information.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Properties	Pollution Control	13B
Coal Gasification		Stationary Sources	13H
Tests		Environmental Assessment	14B
Assessments		Characterization	
Sampling			
Analyzing			

18. DISTRIBUTION STATEMENT
Unlimited

19. SECURITY CLASS (This Report)
Unclassified

20. SECURITY CLASS (This page)
Unclassified

21. NO. OF PAGES
187

22. PRICE mF A01
PC A09

EPA Form 2220-1 (9-73)

EPA-600/7-78-134
July 1978

Guidelines for Preparing Environmental Test Plans for Coal Gasification Plants

by

G.C. Page, W.E. Corbett, and W.C. Thomas

Radian Corporation
8500 Shoal Creek Boulevard
Austin, Texas 78766

Contract No. 68-02-2147
Exhibit A
Program Element No. EHE623A

EPA Project Officer: William J. Rhodes

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

ABSTRACT

The report outlines a philosophy and strategy for preparing environmental assessment sampling and analysis (test) plans. Five major points of test plan development are addressed: (a) defining the test objectives; (b) performing an engineering analysis of the test site; (c) developing a sampling strategy; (d) selecting analytical methods; and (e) defining data management procedures. The important considerations involved in each of these areas are discussed in relation to three types of environmental tests: (a) waste stream (Levels 1, 2 and 3); (b) control equipment; and (c) process stream characterization. Some specific sampling and analytical methods are presented, with numerous references cited for more detailed information.

TABLE OF CONTENTS

Number Page

1.0 INTRODUCTION.................................... 1

2.0 TEST PLAN OBJECTIVES.......................... 4

2.1 WASTE STREAM CHARACTERISTICS............. 5

2.1.1 Screening Waste Streams (Level 1). 6

2.1.2 Detailed Waste Stream Characterization (Level 2)............. 7

2.1.3 Continuous Monitoring of Waste Streams (Level 3)................ 7

2.2 CONTROL EQUIPMENT CHARACTERIZATION....... 7

2.3 PROCESS STREAM CHARACTERIZATION.......... 8

3.0 ENGINEERING ANALYSIS.......................... 10

3.1 GENERAL PRINCIPLES....................... 10

3.1.1 Process Flow Sheet Development.... 11

3.1.2 Process and Waste Stream Characterization................. 14

3.1.3 Definition of Process Variable Effects.......................... 16

3.2 SPECIFIC EXAMPLE - ENGINEERING ANALYSIS OF A CHAPMAN GASIFICATION PLANT......... 17

3.2.1 Process Description.............. 18

3.2.2 Waste Stream Prioritization....... 24

4.0 SAMPLING STRATEGY............................ 29

4.1 SAMPLE POINT SELECTION.................. 30

4.1.1 Sampling Point Selection for Gases 31

4.1.2 Sampling Point Selection for Liquids.......................... 34

TABLE OF CONTENTS (Continued)

Number Page

4.1.3 Sampling Point Selection for Solids 34

4.1.4 Other Sampling Point Considerations 34

4.2 SAMPLING METHOD SELECTION 35

4.3 SAMPLING FREQUENCY AND TIMING 37

4.3.1 Sampling Frequency 37

4.3.2 Sampling Timing 39

4.4 SAMPLING QUALITY CONTROL PROGRAM 40

5.0 ANALYTICAL STRATEGY 45

5.1 SAMPLE HANDLING AND PRESERVATION 52

5.2 ANALYTICAL TECHNIQUES 52

5.2.1 Analytical Screening Techniques ... 53

5.2.2 Quantitative Analytical Procedures 61

6.0 DATA EVALUATION AND MANAGEMENT 88

6.1 PLANNING EXPERIMENTS 88

6.1.1 Statistical Experimental Design ... 89

6.1.2 Quality Control Program 91

6.2 DATA VALIDATION 93

6.2.1 Material Balance Calculations 93

6.2.2 Statistical Data Validation 94

6.3 DATA EVALUATION 94

6.3.1 Waste Stream Characterization Test. 95

TABLE OF CONTENTS (Continued)

Number Page

6.3.2 Control Equipment Characterization Tests 101

6.3.3 Process Stream Characterization Test 103

6.4 DATA HANDLING 103

6.4.1 Manual Data Base Organization 104

6.4.2 Computer Data Base 106

7.0 REFERENCES 107

APPENDIX SAMPLING METHODS 113

A-1 GAS SAMPLING 113

A-2 LIQUID SAMPLING 151

A-3 SOLID SAMPLING 168

A-4 REFERENCES 176

FIGURES

Number		Page
1-1	INTERRELATIONSHIPS AMONG GENERAL AREAS INVOLVED IN PREPARING AN ENVIRONMENTAL TEST PLAN	3
3-1	SIMPLIFIED PROCESS FLOW DIAGRAM - BURNHAM COAL GASIFICATION COMPLEX (REF. 2)	12
3-2	EL PASO BURNHAM GASIFICATION PLANT SECTION (REF. 3)	13
3-3	MODULAR APPROACH TO PROCESS ANALYSIS	17
3-4	SIMPLIFIED PROCESS FLOW DIAGRAM FOR THE CHAPMAN GASIFICATION PLANT..................	20
4-1	NUMBER AND LOCATION OF TRAVERSE POINTS DEFINED BY EPA METHOD 1 GUIDELINES	32
4-2	SAMPLE PORT ARRANGEMENT FOR "HEAD-ON" SAMPLING	33
4-3	EXAMPLE OF A QUALITY CONTROL CHART FOR SPIKED SAMPLES (REF. 5)	42
5-1	OUTLINE OF LEVEL 1 ELEMENTAL ANALYSES USING SPARK SOURCE MASS SPECTROMETRY (SSMS)	55
5-2	LEVEL 1 ANALYSES FOR MERCURY, ANTIMONY AND ARSENIC	56
5-3	OUTLINE OF LEVEL 1 ORGANIC ANALYSES	57
5-4	EXAMPLE INORGANIC ANALYTICAL SCHEME FOR LIQUID SAMPLES	74
5-5a	INTEGRATED SCHEME FOR SEPARATION AND ANALYSIS OF ORGANIC CONSTITUENTS FROM COAL GASIFICATION PROCESSES	86
5-5b	INTEGRATED SCHEME FOR SEPARATION AND ANALYSIS OF ORGANIC CONSTITUENTS FROM COAL GASIFICATION PROCESSES	87

FIGURES (Continued)

Number		Page
6-1	A FULL FACTORIAL DESIGN INVOLVING TWO INDEPENDENT VARIABLES AT THREE LEVELS	90
6-2	EXAMPLE OF A QUALITY CONTROL CHART FOR SPIKED SAMPLES (REF. 5)	92

TABLES

Number		Page
3-1	PROCESS DATA TO BE COLLECTED DURING SAMPLING	28
5-1	ANALYTICAL PARAMETERS OF INTEREST FOR ENVIRONMENTAL TESTING OF COAL GASIFICATION FACILITIES	46
5-2	ENVIRONMENTALLY HAZARDOUS ORGANIC SPECIES POTENTIALLY PRESENT IN COAL GASIFICATION FACILITY PROCESS AND WASTE STREAMS	47
5-3	ORGANIC SPECIES FROM EPA EFFLUENT GUIDELINES (REF. 6)	50
5-4	BIOASSAY PROTOCOL FOR SOLID, LIQUID AND GAS SAMPLES (REF. 1)	51
5-5	ANALYTICAL PARAMETERS FOR SCREENING INORGANIC CONSTITUENTS IN SOLID, LIQUID AND GAS SAMPLES	54
5-6	BIOASSAY PROTOCOL FOR LEVEL 1 WASTE STREAM CHARACTERIZATION TESTS[a]	59
5-7	INORGANIC ANALYTICAL METHODS FOR COAL GASIFICATION PROCESSES (GASEOUS)	64
5-8	INORGANIC ANALYTICAL METHODS FOR COAL GASIFICATION PROCESSES (LIQUIDS)	66
5-9	INORGANIC ANALYTICAL METHODS FOR COAL GASIFICATION PROCESSES (SOLIDS)	70
6-1	LEVEL 1 ORGANIC ANALYSIS RESULTS COMPARED TO MATE VALUES	97
6-2	BIOASSAY TEST RESULTS FOR A COAL GASIFICATION FACILITY	98
6-3	KEY WORD CATEGORIES FOR ENVIRONMENTAL ASSESSMENT DATA BASE	105

ACKNOWLEDGEMENTS

The authors wish to express their thanks to R. V. Collins and J. M. Harless for their contributions to the sampling and analysis sections and to R. A. Magee and M. P. Kilpatrick for their review comments.

SECTION 1.0

INTRODUCTION

This report outlines a philosophy and strategy for preparing environmental assessment sampling and analysis plans (referred to as "test plans" throughout this document) for coal gasification plants. Its primary purpose is to provide general guidelines for the development of conceptually sound site specific test plans. While an environmental test plan may include both source evaluation and ambient monitoring, this report only addresses source evaluation. It is not intended to be a source of the actual procedures required, although many of the applicable sampling and analytical techniques are either referenced or discussed in some detail.

The five general areas which must be addressed in developing an environmental test plan are:

- defining the test objectives,
- performing an engineering analysis of the test site,
- developing a sampling strategy (including selecting sampling points and sample handling methods),
- selecting analytical methods, and defining data management procedures.

The important considerations involved in each of these areas are briefly discussed below.

Any test plan development effort should start with a definitive statement of the anticipated test objectives. This definition is important because it will influence many of the decisions that must be made in the other four areas of test plan design.

An engineering analysis should be performed to identify and characterize the process steps, control equipment, and waste streams associated with a particular site. Ultimately, this analysis should lead to an understanding of the functions and principles of operation of all key pieces of plant hardware, as well as the materials and chemicals involved.

Developing a sound sampling strategy involves addressing such considerations as sample point selection and timing. Obviously, sampling points should be selected so that representative samples of the streams being studied are obtained. The timing and frequency of sampling are usually dictated by the objectives of the test and characteristics of plant operation such as cyclic operations and material residence times.

Sampling methods should be chosen to allow samples from the specified streams to be collected and preserved so that subsequent chemical analysis data are representative of those streams. The physical conditions of the stream, the accuracy requirements of the test, the parameters of interest, and the amount of sample required are important considerations here.

The analytical methods chosen must allow the chemical species of interest to be quantified to acceptable levels of accuracy. Factors affecting analytical method selection include the composition of the stream, the type of sample taken, the sampling method used, and accuracy requirements.

Aspects of the data management function which should be considered in the test planning phase include data validation, data reduction techniques, and data evaluation.

Although each of these areas is distinct, as indicated in Figure 1-1, the decisions which must be made within each are dependent upon limitations inherent within all of the other areas. It is this interdependency in the decision-making process that makes test plan construction difficult. In subsequent sections of this report, each of the five areas just mentioned is discussed in detail. While the individual areas are discussed separately, the need to consider the interrelationships among these areas is stressed.

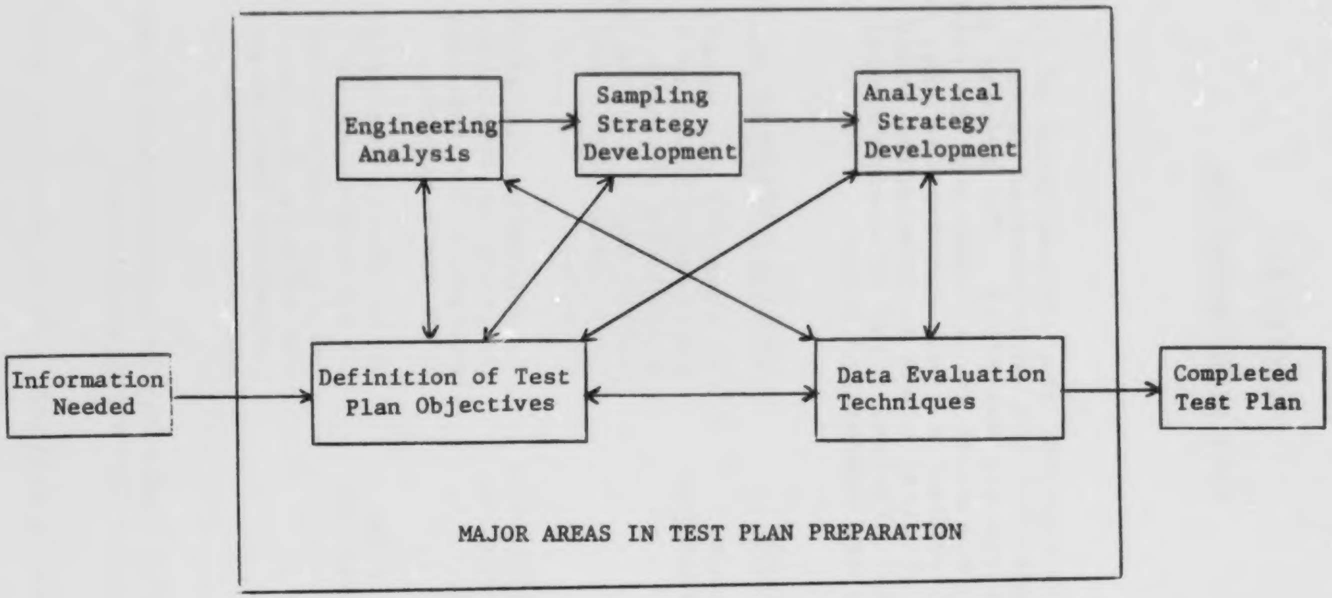

Engineering Analysis
Sampling Strategy Development
Analytical Strategy Development
Information Needed
Definition of Test Plan Objectives
Data Evaluation Techniques
Completed Test Plan
MAJOR AREAS IN TEST PLAN PREPARATION

Figure 1-1. INTERRELATIONSHIPS AMONG GENERAL AREAS INVOLVED IN PREPARING AN ENVIRONMENTAL TEST PLAN

SECTION 2.0

TEST PLAN OBJECTIVES

In this section, the various types of tests which can be used to characterize the environmental aspects of coal gasification technology are described. The primary goal of this discussion is to summarize these tests and the results obtained from each and to emphasize that defining the test objectives is one of the most critical steps in developing sound environmental test plans. Typical types of environmental tests and their objectives are summarized below.

Test Type	General Statement of Test Objectives
Waste Stream Characterization	To identify and quantify the pollutants found in a facility's multimedia (gaseous, liquid, and solid) waste streams and to evaluate their health and ecological effects.
Control Equipment Characterization	To determine the effectiveness of existing or developing control equipment for removing pollutants from waste streams.
Process Stream Characterization	To determine the origins and fates of pollutants as they pass through selected processes and to evaluate the effects that process operating parameters have on pollutant types and concentrations.

The above tests may be executed during one or more of the following process operating conditions:

- normal operation,
- start-up,
- shutdown, and
- emergency upsets.

It is necessary to specify the process operating conditions required since these conditions will affect the physical and chemical characteristics of process and waste streams along with the performance characteristics of control equipment. The desired operating conditions should be defined by the engineering analysis of the plant (or process) to be tested, as discussed further in Section 3.0. The objectives section of an environmental test plan, therefore, should address not only the specific test objectives, but also define the plant operating conditions required.

The following text summarizes the various types of environmental tests (waste stream, control equipment and process stream characterization) and the results that can be obtained from each. Where appropriate, examples are given to help clarify this discussion.

2.1 WASTE STREAM CHARACTERIZATION

A waste stream characterization test is designed to identify and/or quantify the pollutants emitted from a plant or process. The scope of this type of test depends upon the specific test objectives. The Environmental Protection Agency (EPA) has established guidelines for waste stream characterization tests (Ref. 1) which define the following three levels of testing:

- a semiquantitative overview or screening (Level 1),
- an accurate quantification of selected pollutants in selected waste streams (Level 2), or
- continuous monitoring of pollutants in specific waste streams (Level 3).

Typically, Level 1 testing along with an engineering analysis of the plant (as discussed in Section 3.0) can be used to identify environmental problem areas which require more quantitative characterization (Level 2 testing). The results of Level 2 testing can then be used to determine the specific pollutants and streams that require continuous monitoring (Level 3).

A waste stream characterization test may be performed during any of the four plant operation modes (normal conditions, start-up, shutdown, or emergency upsets), although generally it would be performed during normal plant operation. An exception to this would occur when the results of the engineering analysis indicated that there may be significant and/or unique environmental problems associated with the other plant operating modes. In these cases, waste stream characterization tests may be desired during start-up, shutdown, and/or emergency upsets.

The objectives and scope of the three levels of waste stream characterization tests are discussed in the following text. A more detailed discussion of these tests is presented in the IERL-RTP Procedures Manual: Level 1 Environmental Assessment, (EPA-600/2-76-160a and b) (Ref. 1).

2.1.1 Screening Waste Streams (Level 1)

The purpose of a Level 1 waste stream characterization test is to identify gaseous, liquid, and solid waste streams which require further characterization. A Level 1 test, therefore, usually involves screening all of the multimedia waste streams emitted from a plant or process to insure that all possible environmental problem areas are covered.

Although the primary emphasis of a Level 1 test is on waste streams, some process streams such as feedstocks should also be considered because of their effects on the waste stream characteristics and control equipment performance. In a Level 1 test, samples of gaseous, liquid, and solid waste streams are analyzed for organic and inorganic pollutants, biological and ecological effects and particle morphology. Process stream data are also required to determine whether the Level 1 testing occurred during the operating conditions specified by the test plan objectives.

In summary, a Level 1 waste stream characterization test will provide a general overview of the environmental problem areas associated with a facility. The chemical, biological and ecological results from the Level 1 test can then be used to establish priorities for more quantitative characterization testing (Level 2).

2.1.2 Detailed Waste Stream Characterization (Level 2)

The purpose of Level 2 testing is to provide quantitative data for specific pollutants in specific waste streams. As in Level 1 testing, certain process streams should be tested in order to provide information concerning process operating conditions during the test effort.

Level 2 testing is usually too specific and too costly to be performed on all of the waste streams from a plant. Therefore, the results of Level 1 tests and/or an engineering analysis of the plant should be used to identify specific streams for Level 2 testing. If an engineering analysis indicates that an environmental hazard may exist in a particular stream, Level 2 testing can be performed simultaneously with, or in some cases, in lieu of, Level 1 testing. Timing and cost benefits are the important considerations in this decision.

2.1.3 Continuous Monitoring of Waste Streams (Level 3)

The purpose of Level 3 testing is to quantitatively monitor the amounts of specific pollutants found in selected waste streams on a continuous basis. These results should provide data on the relationships between process operation (normal operation, start-up, shutdown and emergency upsets) and the emission rates of specific pollutants. The results from Level 3 testing may also provide guidelines on the specific pollutants and waste streams that require continuous monitoring during plant operation.

2.2 CONTROL EQUIPMENT CHARACTERIZATION

The purpose of a control equipment characterization test is to assess the performance of a control device in treating a specific waste stream and/or to obtain the information required to design the control equipment required to treat a specific waste stream. As for waste stream characterization tests, a control equipment characterization test should be performed during defined plant operating conditions (normal operation, start-up, shutdown, and/or emergency upsets).

In order to assess the performance of a control process, the distributions of specific pollutants or elements of interest in the inlet and outlet streams of the process must be determined. This may also involve performing a material balance test for specified compounds or elements around the control equipment. Material balance tests are usually restricted to selected elements especially if the pollutant in the inlet stream undergoes chemical changes. Therefore, the performance of the control equipment should be assessed both by performing material balances on certain elements and by analyzing specific pollutants in selected inlet and outlet streams.

For example, a Stretford process can be used to control the emissions of gaseous sulfur species from low-Btu gasification plants. The inlet stream to a Stretford process may contain a variety of gaseous sulfur species (H_2S, COS, CS_2, etc.). The outlet sulfur-containing streams consist of by-product sulfur, sulfur species in the blowdown Stretford solution, and gaseous sulfur species in the treated gas and oxidizer vent [illegible]. Therefore, to assess the performance of the Stretford process in controlling sulfur species, an elemental sulfur material balance should be attempted along with determining the concentrations of specific gaseous sulfur species in the inlet and treated gas streams.

The pollutants to be measured in control equipment characterization tests are defined by either the results of waste stream characterization tests or from the results of the engineering analysis. The data collected from these tests should provide guidelines for selecting and/or developing adequate pollution control processes.

2.3 PROCESS STREAM CHARACTERIZATION

The purpose of a process stream characterization test is to provide information on the relationship between process operating parameters (inlet stream composition, temperature, pressure, etc.) and the characteristics of the process waste streams. This type of test is similar to control equipment characterization tests in that performing material balances around the process and/or measuring specific compounds in the process inlet and outlet streams may be required.

An example of a process stream characterization test would be to determine the effect of coal sulfur content on the amount of gaseous sulfur species in the raw low-Btu gas from an atmospheric, fixed-bed gasification process. To accomplish this, an elemental sulfur material balance would be performed around the gasification process along with a measurement of the concentrations of sulfur species in the coal and in the raw product gas. The results of the material balance could be useful in defining an adequate process for removing the gaseous sulfur species (H_2S, COS, CS_2, etc.) found in a typical raw product gas stream.

In summary, there are various types of environmental tests that can be performed to accomplish specified environmental objectives. Waste stream characterization can be associated with a plant (or a process) or used to define needs for specific control equipment. Control equipment characterization is useful in evaluating the effectiveness of equipment used for treating process waste streams. Process stream characterization is useful in determining the relationships between process operating parameters and process waste stream characteristics.

It must be emphasized that while performing any of these environmental tests, the plant operating conditions (normal operation, start-up, steady-state, and emergency upsets) must be defined. These desired plant conditions should be determined by performing an engineering analysis of the plant.

SECTION 3.0

ENGINEERING ANALYSIS

In this section, the general principles involved in performing an engineering analysis of a candidate gasification plant test site are discussed. Application of the principles discussed is illustrated by a specific example.

3.1 GENERAL PRINCIPLES

An engineering analysis should provide a sound basis for translating a set of general test objectives into a set of specific process data needs. The element which is fundamental to any engineering analysis is the development of an accurate understanding of the functions of all environmentally significant process operations within a plant. The specific steps which would usually be involved in developing this understanding include:

- constructing an up-to-date plant flow sheet showing all process and emission streams which are relevant to the objectives of the test program,
- characterizing the process and waste streams of interest with respect to their flow rates, compositions, and physical characteristics, and
- identifying (and defining the normal operating levels of) process variables which affect the characteristics of the process or waste streams being considered.

The important factors involved in each of these areas are addressed in the following sections.

3.1.1 Process Flow Sheet Development

The development of an up-to-date process flow sheet is a necessary first step in any engineering analysis because it provides a convenient mechanism for identifying:

- the major processing steps and equipment items found at a given facility,
- the input and output (including waste streams) associated with each equipment item, and
- the process characteristics which might be expected to have an impact on waste stream properties.

Depending on the complexity of the facility in question, it may be possible to represent the whole plant on a single flow sheet, or it may be necessary to use several sheets. An example of a relatively simple facility is the gasification plant which is described later in this section. Extremely complex facilities such as the conceptual El Paso Burnham gasification plant are best handled by: 1) breaking the overall plant into sections (see for example, Figure 3-1), and 2) presenting individual flow diagrams for the various sections. Figure 3-2, which shows the processing units associated with the Burnham plant gasification section, is indicative of the level of detail which is desired on a test plan process flow sheet.

In most cases, existing plant flow diagrams (*e.g.*, piping and instrumentation diagrams) can be used as a basis for constructing suitable flow diagrams for test planning purposes. In cases where this type of resource is not available, a flow diagram should be constructed from information gathered during a preliminary site screening visit.

The importance of a site visit in terms of its potential value to a test planning effort cannot be emphasized enough. In order to derive the maximum possible benefit from a site visit, it should be recognized that a number of information needs should be addressed during a site visit.

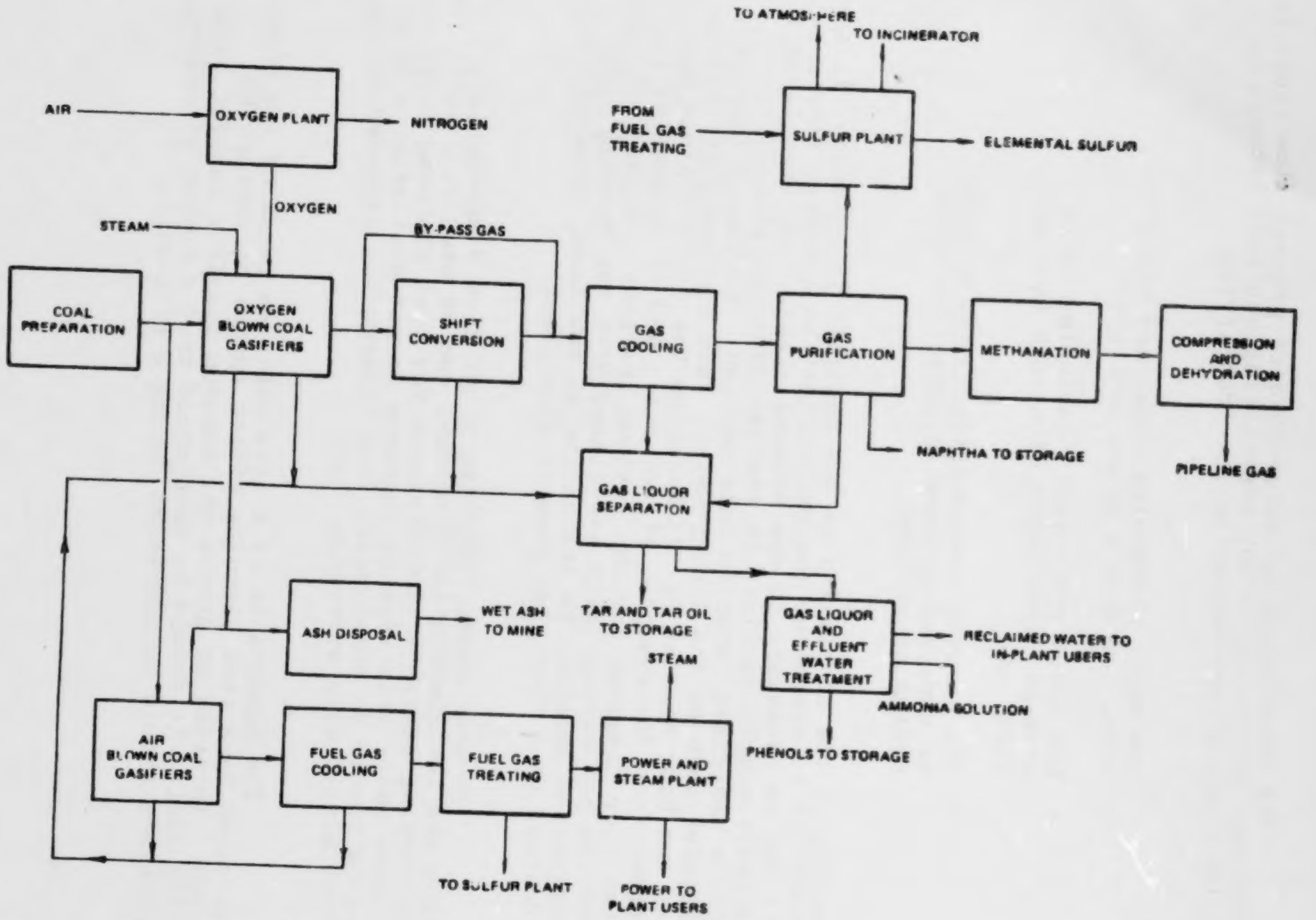
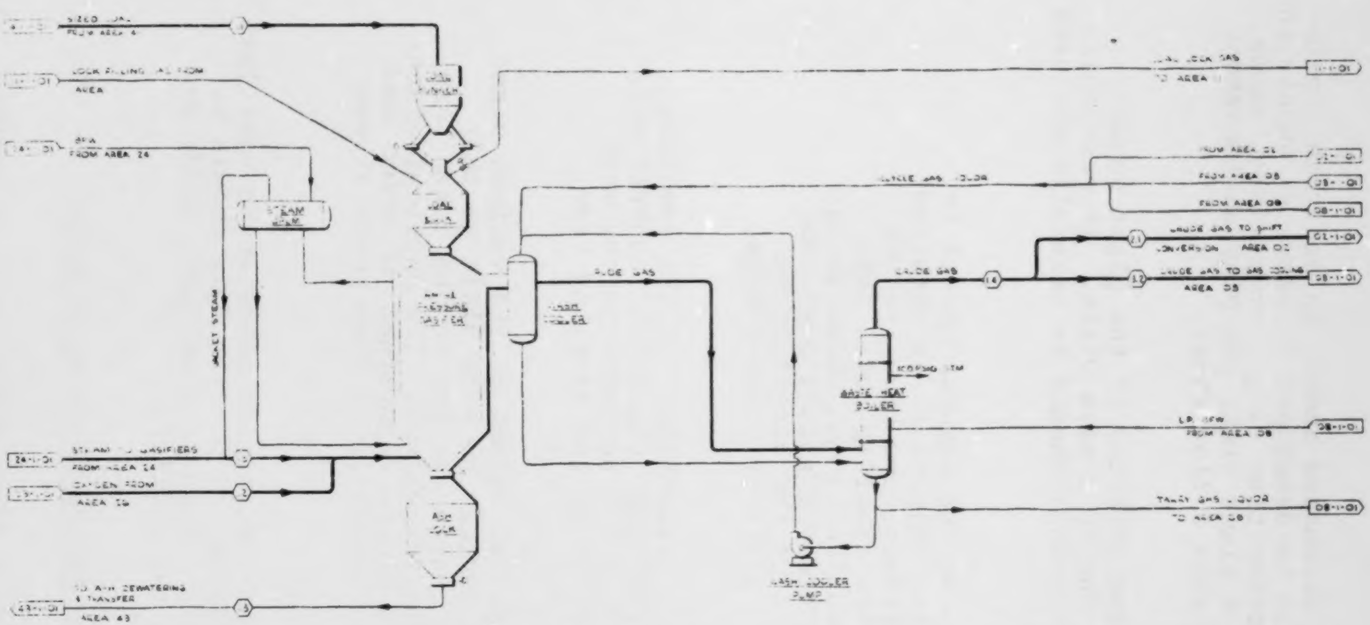

TO ATMOSPHERE
TO INCINERATOR
AIR
OXYGEN PLANT
NITROGEN
FROM FUEL GAS TREATING
SULFUR PLANT
ELEMENTAL SULFUR
OXYGEN
STEAM
BY-PASS GAS
COAL PREPARATION
OXYGEN BLOWN COAL GASIFIERS
SHIFT CONVERSION
GAS COOLING
GAS PURIFICATION
METHANATION
COMPRESSION AND DEHYDRATION
NAPHTHA TO STORAGE
PIPELINE GAS
GAS LIQUOR SEPARATION
ASH DISPOSAL
WET ASH TO MINE
TAR AND TAR OIL TO STORAGE
GAS LIQUOR AND EFFLUENT WATER TREATMENT
RECLAIMED WATER TO IN-PLANT USERS
AMMONIA SOLUTION
STEAM
PHENOLS TO STORAGE
AIR BLOWN COAL GASIFIERS
FUEL GAS COOLING
FUEL GAS TREATING
POWER AND STEAM PLANT
TO SULFUR PLANT
POWER TO PLANT USERS

Figure 3-1. SIMPLIFIED PROCESS FLOW DIAGRAM - BURNHAM COAL GASIFICATION COMPLEX (REF. 2)


SIZED COAL FROM AREA 4
LOCK FILLING GAS FROM AREA
BFW FROM AREA 24
STEAM TO GASIFIERS FROM AREA 24
OXYGEN FROM AREA 26
TO ASH DEWATERING & TRANSFER AREA 43
COAL BUNKER
COAL LOCK
STEAM DRUM
JACKET STEAM
PRESSURE GASIFIER
ASH LOCK
WASH COOLER
WASH COOLER PUMP
CRUDE GAS
WASTE HEAT BOILER
CYCLE GAS LIQUOR
COAL LOCK GAS TO AREA 11
FROM AREA 02
FROM AREA 08
FROM AREA 08
CRUDE GAS TO SHIFT CONVERSION AREA 02
CRUDE GAS TO GAS COOLING AREA 03
L.P. BFW FROM AREA 08
TARRY GAS LIQUOR TO AREA 08
21
12
14
1
2
3
5

STREAM NUMBER			1		2		3		14		15		21		12	
COMPONENT	MOL. WT.	HHV	MOLS/HR	VOL %	MOLS/HR	VOL %	MOLS/HR	VOL %	MOLS/HR	VOL %	MOLS/HR	VOL %	MOLS/HR	VOL %	MOLS/HR	VOL %
1 CO₂	44.010				–	–			30,300.0	28.03			16,568.0	28.03	13,732.0	28.03
2 H₂S	34.082	639			–	–			[illegible]	.37			217.2	.37	180.0	.37
3 C₂H₄	28.052	604			–	–			437.5	.40			239.2	.40	198.3	.40
4 CO	28.010	322			–	–			21,837.8	20.20			11,940.9	20.20	9,896.9	20.20
5 H₂	2.016	325			–	–			42,092.[illegible]	38.95			23,016.4	38.95	19,076.5	38.95
6 CH₄	16.043	1012			–	–			12,031.4	11.13			6,578.8	11.13	5,452.6	11.13
7 C₂H₆	30.068	1773			–	–			656.2	.61			358.8	.61	297.4	.61
8 N₂ + Ar	28.020	–			299.6	2.00			338.9	.31			185.3	.31	153.6	.31
9 O₂	32.000	–			14,38[illegible].4	98.00			–	–			–	–	–	–
10 TOTAL DRY GAS					14,680.0	100			108,081.9	100			59,104.6	100	48,987.3	100
11 MOLE. WT. (DRY GAS)			——		32.06		——		21.10		——		21.10		21.10	
12 TOTAL DRY GAS (LBS/HR)			——		470,440		——		2,280,477		——		1,246,945		1,033,902	
13 WATER			314,450		——		——		394,960		1,783,540		762,764		632,196	
14 COAL (MAF)			1,150,300		——		19,459		——		——		——		——	
15 ASH			378,210		——		378,210		——		——		——		——	
16 NAPHTHA			——		——		——		20,005		——		10,939		9,[illegible]	
17 TAR OIL			——		——		——		28,007		——		3,314		2,693	
18 TAR			——		——		——		7,314		——		3,999		3,315	
19 CRUDE PHENOLS			——		——		——		9,127		——		4,991		4,136	
20 NH₃			——		——		——		1,629		——		9,640		7,989	
21																
22																
23 TOTAL LBS/HR			1,758,480		470,440		397,669		3,757,489		1,783,540		2,064,592		1,702,897	
24 MMSCFD (DRY)			——		133.4		——		982.2		——		537.1		445.1	
25 HHV (BTU/SCF DRY)			——		——		——		323.4		——		323.4		323.4	

Figure 3-2. EL PASO BURNHAM GASIFICATION PLANT SECTION (Ref. 3)

Reproduced from best available copy.

First of all, as discussed above, an accurate, up-to-date plant flow sheet should be developed to serve as an aid in establishing test program priorities (*e.g.*, objectives, scope, sampling strategy, etc.). A plant visit can play an important role in the development of such a flow sheet.

The physical characteristics of the plant should receive specific attention during a site visit. In particular potential sampling point locations should be carefully screened, taking into consideration:

- Suitability - can the samples needed to fulfill the test objectives be obtained? Important considerations here include existing vs. new sampling port, port size, port location (*e.g.*, relative to upstream/downstream obstructions), and characteristics of the stream to be sampled (*e.g.*, pressure, temperature, flow velocity).
- Accessibility - availability of the sampling platforms/scaffolding, electrical connections, etc. needed to safely accommodate the work space requirements of the sampling team.

The sizes and physical layout of the various plant components should be noted during the site visit so that appropriate residence time considerations can be taken into account in planning the sampling effort. The physical dimensions of lines and ducts should be determined in order that average flow velocities can be estimated from known stream volumetric flow rates .

In addition to the information needs which were just discussed, a considerable amount of process data should be gathered during a site visit. Some of these data needs are addressed in the following two sections.

3.1.2 Process and Waste Stream Characterization

Once the basic plant flow scheme has been defined, all environmentally significant process and waste streams shown on the flow sheet should be characterized with respect to their flow rates, compositions and physical characteristics. Obviously, an environmental test program will tend to focus on waste streams rather than process streams. However, in many cases, certain process stream characteristics will be of interest because of their effects upon the waste streams produced in downstream processes.

It is very important to consider the need for gathering accurate process characterization data during a preliminary site screening visit. Some of the reasons for this are as follows:

- Quite frequently, published process data such as that shown on process flow sheets (see Figure 3-2, for example) will reflect design or average, rather than actual process conditions.
- An appreciation for the variability of the process can be gained by observing its operation, by reviewing plant operating logs and by discussing the magnitudes of and the driving forces for those variations with the plant operators.

Another issue which should be addressed during the site visit is the availability of desired process monitoring instrumentation. Generally, an operating plant will not be equipped with all of the instrumentation needed to fully characterize the operation of the process. Particularly in a commercial plant it would be more typical to find that the minimum number of process monitors needed to safely control the process would be used. A developmental or demonstration unit would tend to be better instrumented.

Available data on stream characteristics should be considered in an engineering analysis to provide a basis for establishing test priorities. If time and/or budget constraints exist, it will generally be reasonable to concentrate test program efforts on:

- the most environmentally significant streams in terms of their mass emission rates of specific hazardous compounds or classes of compounds,

- the streams which are the most applicable to broad rather than specialized areas of a technology, and

- the streams about which the least is known.

Some of the important considerations involved in each of these areas are addressed in the example which is discussed in Section 3.2.

3.1.3 Definition of Process Variable Effects

This task addresses one of the more difficult areas in test plan construction and in some cases may be beyond the test plan scope. The proper execution of this task requires a thorough understanding of the plant and its component processes. Once this understanding is gained, however, specifying the variables which would be expected to affect the characteristics of potential waste streams is reasonably straightforward. Ultimately, this effort should also provide a basis for defining what process data should be collected in conjunction with the execution of the task so that subsequent analyses of the test results will yield useful correlations.

The recommended approach to addressing the problems inherent in this task is a multifaceted one. First of all, available data from the candidate site should be evaluated. Applicable information from other sites or from related technology areas should also be considered to determine which process variables would be expected to have the major impacts on the facility's waste stream characteristics.

A modular type of analysis (symbolically represented in Figure 3-3) is a useful way to approach this problem. In simple terms this approach involves defining the expected characteristics of the waste stream from a process or group of processes in terms of their input stream characteristics and operating parameters. In theory, an entire plant could be analyzed using this approach. However, it is probably more reasonable to start with an application of this technique to the specific equipment items from which the various plant waste streams originate.

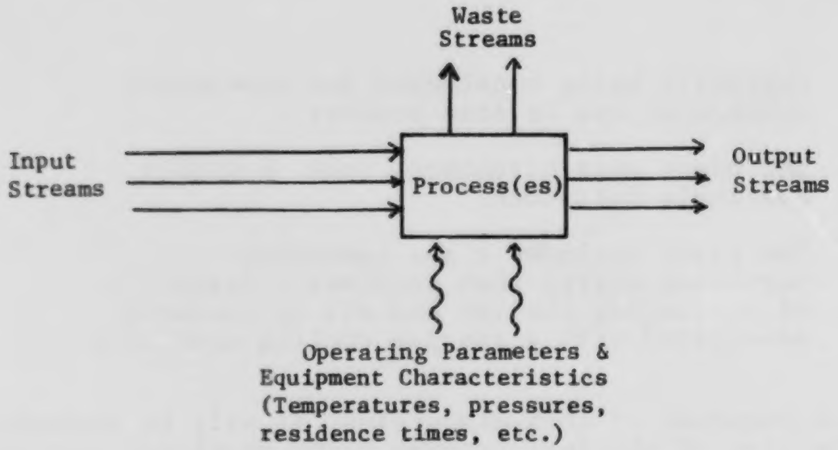

Waste Streams
Input Streams
Process(es)
Output Streams
Operating Parameters & Equipment Characteristics (Temperatures, pressures, residence times, etc.)

Figure 3-3. MODULAR APPROACH TO PROCESS ANALYSIS

The discussion which has been presented to this point has described in general terms the major tasks involved in an engineering analysis. The following section illustrates how these techniques can be applied to a specific gasification facility.

3.2 SPECIFIC EXAMPLE - ENGINEERING ANALYSIS OF A CHAPMAN GASIFICATION PLANT

The Chapman gasification plant selected for this example is an actual facility which was tested as part of Radian's low-Btu gasification technology data acquisition program. This facility was selected as a test site for the low-Btu program for the following reasons:

- It is one of only a few commercial-scale gasification units which is operating in this country.
- The facility has a well-defined operating history.
- It uses fixed-bed, atmospheric pressure, single-stage gasifiers which are representative of the gasifier type which is

currently being considered for widespread commercial use in this country.

- The plant uses bituminous coal, a widely available feedstock.
- The plant includes a gas quenching-scrubbing system that provides a means of evaluating the tar and oil by-products associated with a raw gas cooling operation.

For purposes of this discussion, it will be assumed that the objective of the test program being developed here will be to characterize the emission streams leaving the Chapman facility. The first step to be followed in the pursuit of this objective involves the development of an accurate description of the facility, including:

- a process flow sheet showing all significant process and waste streams, and
- a discussion of the significant operating characteristics of the plant, with emphasis on the factors which affect the characteristics of the plant's waste streams.

It should be noted that the following section was generated from information gathered during a preliminary visit to the Chapman site. The discussion presented here is representative of the level of understanding needed to make reasonable test program decisions.

3.2.1 Process Description

The coal gasification facility discussed in this example produces low-Btu gas which is used as a process furnace combustion fuel. While twelve Chapman gasifiers are operational at this facility, only two gasifiers are operated at any one time to meet current fuel demands.

Four processing operations are used in the plant: (a) coal handling; (b) gasification; (c) gas purification, which includes particulate removal and gas quenching and scrubbing; and d) water (process condensate) treatment. A process flow sheet for the Chapman gasification unit is presented in Figure 3-4. This diagram also shows the air, water, and solid waste streams associated with each process operation. In the following text, each of these operations and their respective multimedia waste streams are discussed in more detail.

Coal Handling -

The coal handling operation at the Chapman facility consists of: a) delivery/storage of presized Virginia bituminous coal in hopper cars, b) conveying, and c) storing this coal in the gasifier feed hoppers. No coal grinding, crushing, sizing, or drying operations are used at the plant site.

The major waste streams associated with the coal handling operation are particulates from coal conveying and coal storage. The compositions of these emitted particulates should be similar to that of the coal feedstock.

Gasification -

The gas producers are single-stage, atmospheric, fixed-bed, air-blown Chapman gasifiers. The coal feedstock enters the top of the gasifiers through a barrel valve and is spread across the bed by a distribution arm. Steam and air introduced into the bottom of the gasifier pass through a grate which evenly distributed these gases and also supports the coal bed. Ash from the gasifier is collected in a water sealed ash pan and removed from the unit using an ash plow. The hot raw gas exits the top of the gasifier at 840-940°K (1050-1250°F) and enters a cyclone to remove entrained particulates (ash and coal dust). Pokeholes located on top of the gasifier are positioned so that rods can be periodically inserted to break up any coal agglomerates which form.

The discharge streams associated with the gas production operation are: a) gaseous emissions from the barrel valve, pokeholes, and leaks around the gasifier seals; and b) moist ash exiting the bottom of the gasifier. These gaseous emissions are released to the atmosphere.

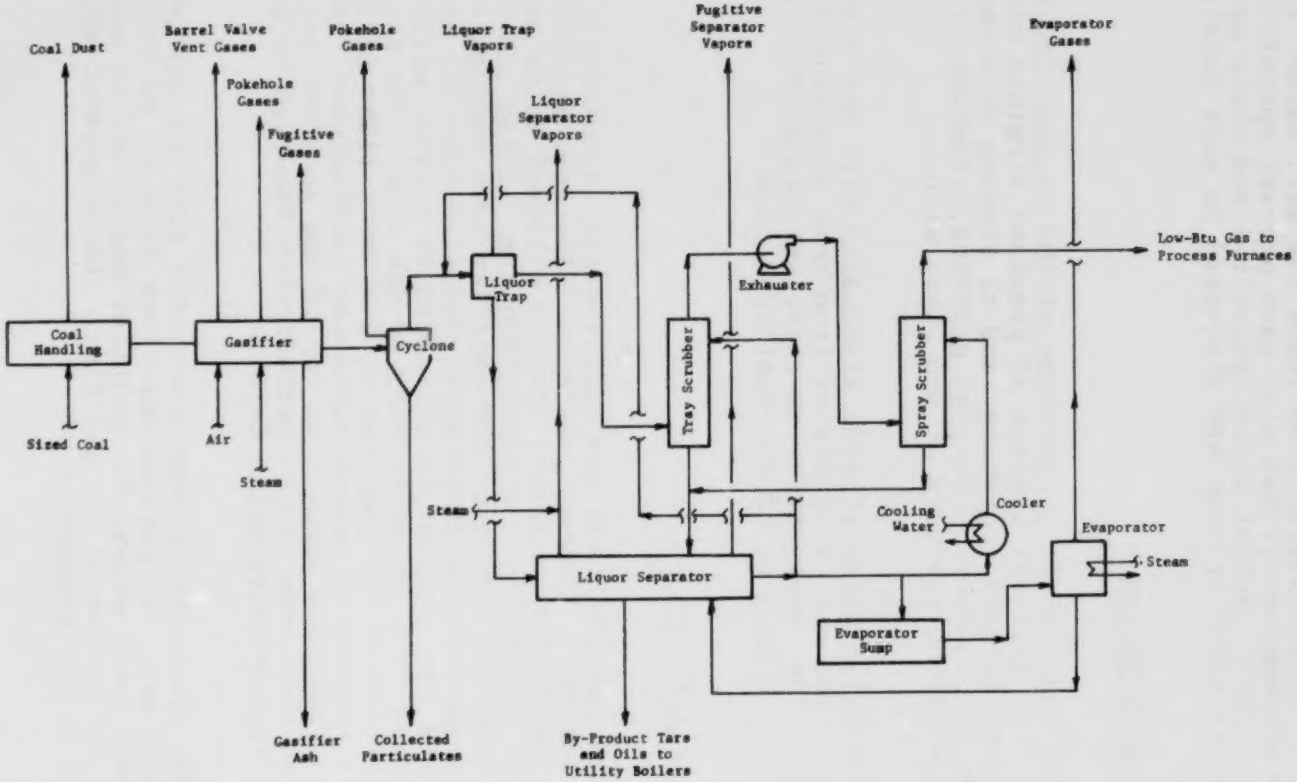

Coal Dust
Barrel Valve Vent Gases
Pokehole Gases
Fugitive Gases
Pokehole Gases
Liquor Trap Vapors
Liquor Separator Vapors
Fugitive Separator Vapors
Evaporator Gases
Low-Btu Gas to Process Furnaces
Coal Handling
Gasifier
Cyclone
Liquor Trap
Exhauster
Tray Scrubber
Spray Scrubber
Sized Coal
Air
Steam
Steam
Cooling Water
Cooler
Evaporator
Steam
Liquor Separator
Evaporator Sump
Gasifier Ash
Collected Particulates
By-Product Tars and Oils to Utility Boilers

Figure 3-4. SIMPLIFIED PROCESS FLOW DIAGRAM FOR THE CHAPMAN GASIFICATION PLANT

Gas Purification -

The gas purification operation at the Chapman facility consists of the following steps:

- particulate removal, and
- quenching and scrubbing.

These steps are described in the following sections.

Particulate Removal -

Particulate removal is accomplished in a hot, refractory lined cyclone that operates at a temperature slightly lower than the gasifier overhead temperature. Each gasifier is equipped with its own cyclone. The particulates removed by the cyclones consist of coal dust, ash and tar entrained in the raw gas. These particulates collect at the bottom of each cyclone. Pokeholes are located in the top of each cyclone and in the hot gas ducts so that steam lances can be periodically inserted to break up agglomerated particulates.

Atmospheric emissions from the cyclones consist of pokehole vent gases and leaks. The collected particulates, which constitute a solid waste stream, are combined with the gasifier ash for disposal.

Quenching and Scrubbing -

The hot gas leaving the cyclones is quenched by a series of sprays located inside the exit lines from each cyclone. Excess quench water is collected in a series of liquor traps (one trap to each gasifier/cyclone). The gas from all operating liquor traps enters a collecting main. Water sprays located inside this main cool the gas to approximately 340°K (150°F). Excess tar and quench liquor from both the liquor traps and the collecting main are directed to the liquor separator. Pitch which accumulates in the liquor traps is periodically collected and disposed of off-site.

After the initial quenching step, the gas is scrubbed and further cooled in two tray scrubbers which are operated in parallel. In this operation most of the tars, oils, and particulates are removed as the gas is cooled to approximately 330°K (135°F).

The gas exiting these tray scrubbers is combined and compressed before entering the final spray scrubber. In this spray tower, some residual tars, oils, and particulates are removed as the gas is further cooled to 320°K (120°F). The effluent liquor from both the spray and tray scrubbers is returned to the liquor separator.

The liquor separator at the plant is a large concrete tank (approximately 5 x 13 x 2 meters). Process condensate and any condensed tars and oils from the quenching/scrubbing steps described above enter at one end of the tank. A series of baffles is used to minimize the turbulence caused by the incoming liquor and to keep oils and tars which have settled to the bottom of the separator from entering the clean liquor uptake line. The tars and oils which accumulate in the separator are burned as an auxiliary fuel in a coal fired boiler. The water is recirculated to the quenching and scrubbing operations.

The discharge streams from this operation include fugitive emissions from the liquor traps, and vent gases from the liquor separator. A steam ejector is used to vent the vapor space above the liquor in the separator.

Water Treatment -

Water treatment problems are minimized at the Chapman facility by operating the gasification process such that there is no net accumulation of water. If excess water accumulates, it is evaporated. Air emissions from the evaporator should contain volatile materials found in the condensate.

Waste Stream Summary -

Potential waste streams identified in the Chapman gasification facility include:

Gaseous Emissions

- Barrel valve vent gases
- Fugitive emissions from the gasifier and cyclone pokeholes
- Gas/liquor trap vapors
- Liquor separator vapors
- Evaporator vapors
- Stack gases from the process heaters
- Particulates from coal conveying and storage operations

Liquid Effluents

- By-product tars and oils

Solids Wastes

- Gasifier ash
- Collected particulates (cyclone)
- Pitch from liquor traps
- Sludge from liquor separator

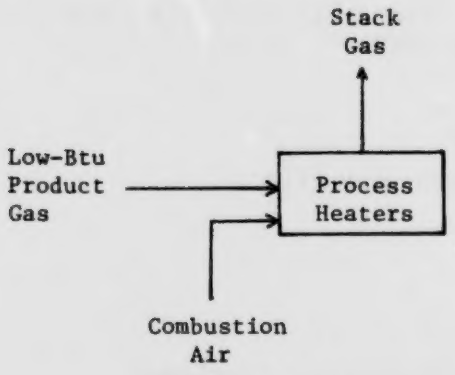
These discharge streams and their expected compositions can be summarized in general terms as follows.

The compositions of the pokehole, and barrel valve vent gases should be similar to that of the raw gas exiting the gasifier. The gaseous emissions from the liquor trap, liquor separator and evaporator should contain a wide range of volatile inorganic and organic compounds most of which should be found in the condensate or tar/oil fraction as well. The only liquid effluent from the Chapman gasification plant is the by-product tar and oil stream. The four types of solid wastes identified above would all be fairly unique materials.

3.2.2 Waste Stream Prioritization

Gas Streams -

On a gross emission rate basis, the process heater stack gas is the most significant gaseous emission stream at the Chapman facility. The concentrations of specific hazardous components present in the stack gas should be small, however.

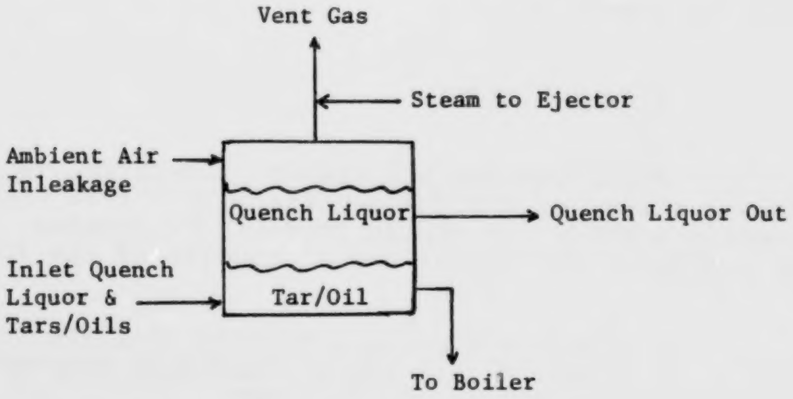


The fates of environmentally hazardous low-Btu product gas components in a combustion process is of interest to the program. Certainly, most of the organic materials present in the product gas should be oxidized to less harmful flue gas components in a combustion process. However, it would probably be reasonable to screen the stack gas using waste stream characterization (Level 1) sampling and analysis procedures. Then, if positive indications of harmful levels of specific components were obtained, subsequent studies to more fully characterize the stack gas would be justified. These studies might entail defining the emission rates of specific flue gas components as functions of the input fuel gas composition and the operating characteristics (*e.g.*, excess air firing rate) of the furnaces.

The characteristics of the barrel valve vent gas should be determined by direct sampling. This should be done to determine the extent to which raw gas components such as tars are sorbed by the coal feed.

The characteristics of the various fugitive emissions could be determined most efficiently by sampling the raw gasifier product gas. If emission rate estimates indicated that those streams were a significant emission source, an attempt should be made to measure the rates and compositions of those emissions directly.

The liquor separator vent is another significant gaseous emission stream. Simultaneous sampling and subsequent analyses of both the vent stream and the separator liquor are desirable here since this should provide a basis for relating the composition of the vent gas to levels of volatile materials found in the separator liquor.


Vent Gas
Steam to Ejector
Ambient Air Inleakage
Quench Liquor
Quench Liquor Out
Inlet Quench Liquor & Tars/Oils
Tar/Oil
To Boiler

It would not be recommended that any significant time or effort be devoted to the characterization of particulate emissions from the coal handling operations at the Chapman plant. This is because:

- these emissions are not unique to a gasification plant, and
- adequate characterization data for this type of emission source already exist in the literature.

Evaporator vent gases would not need to be sampled for the following reasons.

- This is an intermittent stream which is generated only when the evaporator is operated (which, in theory, is infrequently).

- The characteristics of this stream should be similar to those of the separator vent.

Likewise, gas/liquor trap vapors would not be recommended for sampling because the components in this stream should be similar to those encountered in the liquor separator vent stream. A method of estimating the flow rate of this stream, however, should be investigated.

Liquid Streams -

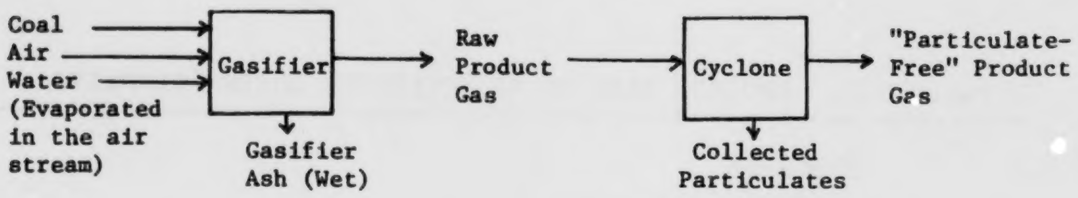
While the tar/oil stream, literally, is not an effluent stream at the Chapman facility (it is stored and subsequently burned), it should probably be sampled. The analysis data gathered for the tar should consist of the following:

- a broad organic screening analysis to identify classes of hazardous compounds present in the tar, and

- a detailed characterization of the light ends fraction since this would help to define the expected composition of potential storage tank vent gases.

Analysis of the tar/oil stream would also provide a basis for defining the distributions of key pollutants (NH_3, sulfur species, cyanides, trace metals, etc.) between the aqueous and the organic layers in the liquor separator.

Solid Waste Streams -


Coal
Air
Water (Evaporated in the air stream)
Gasifier
Gasifier Ash (Wet)
Raw Product Gas
Cyclone
Collected Particulates
"Particulate-Free" Product Gas

The gasifier ash and the collected particulates exiting the bottom of the gasifier and the cyclone, respectively, should clearly be sampled and characterized using Level 1 procedures because these are the two major solid waste streams produced at the Chapman facility. The flow rates of these streams should also be determined.

Samples of the liquor trap pitch and the liquor separator sludge should also probably be analyzed to determine the significance of these materials as potential sinks for certain pollutants (heavy metals, for example). Net production rates for these materials would have to be estimated based on information obtained from the plant operating staff, *i.e.*, the frequency of cleanup and the quantity of material removed.

The operating data that should be collected during these tests are presented in Table 3-1. These data will be used in conjunction with the results of the sampling task to perform an engineering analysis of the plant's performance and to insure that the plant is operating at desired conditions when the samples are collected.

Table 3-1. PROCESS DATA TO BE COLLECTED DURING SAMPLING

Gasifier

- Coal feed rate
- Pressure
- Air flow rate, temperature and moisture content
- Outlet gas temperature and flow rate
- Ash flow rate and temperature

Cyclone

- Overhead temperature
- Accumulation rate of collected particulates

Tray Scrubbers

- Inlet gas temperature and flow rate
- Outlet gas temperature and flow rate
- Inlet liquor temperature and flow rate
- Outlet liquor temperature and flow rate

Separator

- Tars/oils - net production rate

Spray Scrubber

- Inlet gas temperature and flow rate
- Outlet gas temperature and flow rate
- Inlet liquor temperature and flow rate
- Outlet liquor temperature and flow rate

Quench Water

- Inlet temperature and flow rate
- Outlet temperature and flow rate

Product Gas

- Temperature and flow rate

SECTION 4.0

SAMPLING STRATEGY

In this section, the selection and execution of sampling procedures to be used in producing reliable waste stream, control equipment, and process stream characterization data are discussed. In developing a sampling strategy for an environmental test, the following items should be addressed:

- sampling point selection, including location,
- sampling methods selection,
- sampling frequency and timing, and
- sampling quality control program.

The selection of sampling points and methods should be based upon the accuracy requirements of the test, the physical condition of the stream to be sampled (*e.g.*, temperature and pressure), analytical requirements with respect to sample size or sample pretreatment requirements, the expected chemical composition of the stream, potential component reactivities (sample stability and safety considerations), and the physical arrangement of piping and ducting containing the stream to be sampled. Other considerations may include sampling practices of plant personnel, effects of sampling on plant operation, and safety and work area constraints.

Sampling frequency and timing involve decisions on how often to sample and when to sample, respectively. Sampling frequency constraints include the sampling method itself, plant operational variations, quality control requirements, and data evaluation needs. Sampling timing is process dependent and is defined by the desired plant operating conditions (normal operation, start-up, shutdown, and upsets) and the type of environmental test (waste stream, control equipment, and process stream characterization) being performed.

A sampling quality control program should be used to insure that the data collected during the environmental test are both accurate and precise. This program should include the following elements:

- calibrating sampling and analytical equipment,
- taking replicate samples,
- performing replicate analyses,
- using alternative (if available) sampling and analytical methods,
- comparing with plant personnel obtained values, and
- establishing a clearly defined chain of responsibility for sample collection, sample analysis, and evaluation of the results.

In the following text, each of the four major areas involved in developing a sampling strategy is discussed. Specific sampling methods are presented in the Appendix. Examples are also given to illustrate how and why these items are incorporated into an environmental test plan.

4.1 SAMPLE POINT SELECTION

The process considerations for sampling point selection (including process stream selection and accessibility) are discussed in the Engineering Analysis Section (Section 3.0). This section is concerned primarily with selecting the actual sampling point locations and focuses upon problems related to stream flow characteristics.

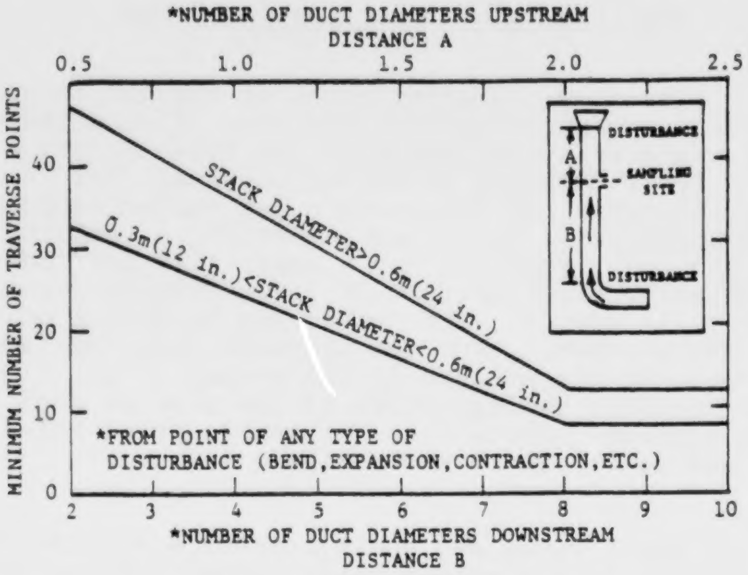
In the following text, methods for selecting sampling points for gases, liquids and solids are presented.

4.1.1 Sampling Point Selection for Gases

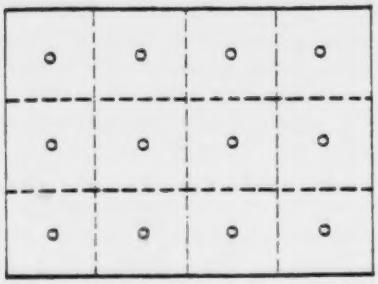
The flow characteristics of the gas stream to be sampled are a basic consideration that affects the ease with which a representative sample of the total stream can be collected. EPA's Method 1 guideline document (Ref. 4) presents specific criteria for selecting a gas stream sampling port. The EPA approach is based upon selecting a sampling location having minimum turbulence and a capability for traversing a representative cross section of the stream to provide a statistically valid sample. The number and locations of the traverse points are dependent upon the distance from the sampling point to the nearest disturbance in the stream (*e.g.*, elbow or tee) and the specific configuration of the pipe or duct containing the gas streams. Guidelines for sample point selection for stacks and ducts are shown in Figure 4-1.

Small pipes and ducts present a special problem in the selection of a sampling point. The traverse approach of Method 1 requires that the sampling port (or ports) be constructed at a right angle to the direction of flow. This allows traverses across the stream's cross-sectional area to be made. For small pipes, the sampling port itself may be a source of turbulence. As a general rule, if the cross-sectional area of the required sample port is greater than one-fifth of the cross-sectional area of the pipe to be sampled, the port should not, if possible, be constructed at the proposed sampling point. The alternative recommended is to find a section of pipe having a minimum length of 10 pipe diameters and terminating downstream in an elbow. The sampling port should then be constructed in the elbow such that a probe can be inserted into the center of the stream at a distance of two pipe diameters upstream of the elbow (see Figure 4-2). The probe's cross-section should be less than one-fifth of the pipe's cross-sectional area to avoid significant turbulence caused by the probe.

The previous discussion presents the criteria which apply to ideal sampling point locations. However, for certain environmental tests, such as a Level 1 waste stream characterization test, the accuracy requirements (within a factor of ±2) are such that installing new sampling ports may not be justified. This is particularly true when there are existing sampling ports in the pipe or duct. A judgment must then be made whether the existing sample port locations will meet the accuracy requirements of the environmental test.

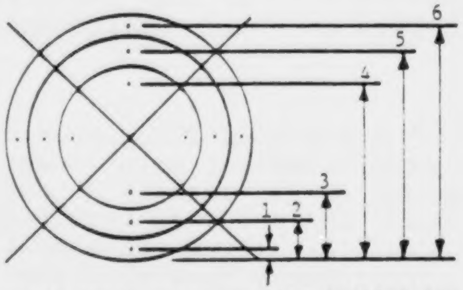


Minimum number of traverse points.



Example showing rectangular stack cross section divided into 12 equal areas, with traverse points at centroid of each area.

TRAVERSE POINT	DISTANCE % of diameter
1	4.4
2	14.7
3	20.5
4	70.5
5	85.3
6	95.6



Example showing circular stack cross section divided into 12 equal areas, with location of traverse points at centroid of each area.

Figure 4-1. NUMBER AND LOCATION OF TRAVERSE POINTS DEFINED BY EPA METHOD 1 GUIDELINES. (Ref. 4)

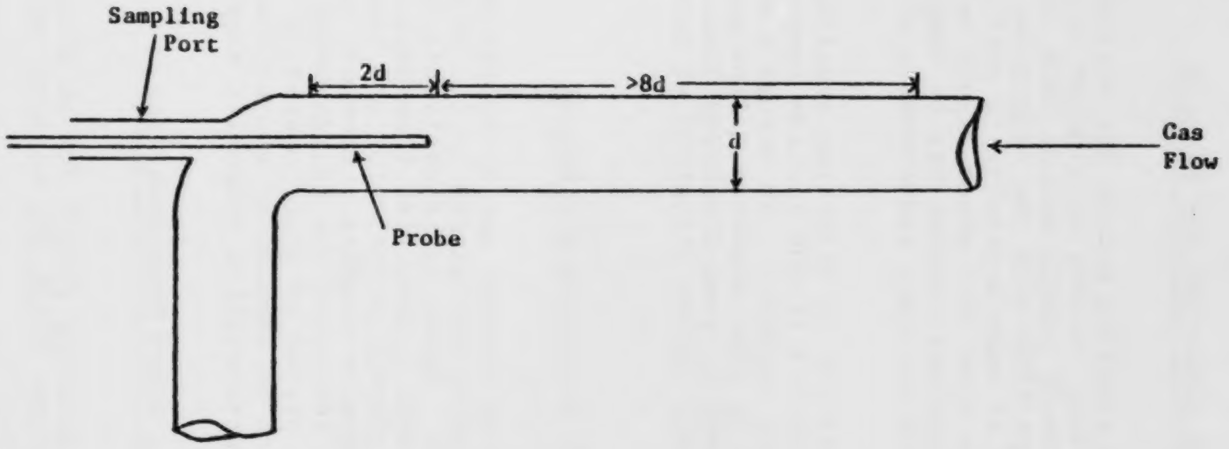

Sampling Port
2d
>8d
d
Gas Flow
Probe

Figure 4-2. SAMPLE PORT ARRANGEMENT FOR "HEAD-ON" SAMPLING

4.1.2 Sampling Point Selection for Liquids

The preferred sampling points for enclosed liquid streams are existing valves, either in-line or on a side stream. These valves provide a ready sample source from the stream and should be used when compatible with the objectives of the test program. Another point of easy access is at outflow orifices where the liquid streams flow into ponds, tanks or other open vessels. Open or noncontained streams may be sampled at any point compatible with the accuracy requirements of the test.

A major restriction in selecting sampling points is stream homogeneity, particularly for liquids composed of mixed phases (*e.g.*, aqueous and organic). To ensure a well-mixed sample, sampling should be done downstream from points of turbulence, such as elbows or pump-discharge lines. It may be necessary to have sampling valves installed at points where none exist.

4.1.3 Sampling Point Selection for Solids

Samples of solid streams may be collected from storage piles or bins, transport containers (*e.g.*, trucks and railroad cars), or conveyors. Often it is desirable to composite solid samples obtained over a specified time period. Generally, samples collected from storage piles, bins and transport containers are already composite samples. However, samples obtained from conveyors represent the solids being used or produced during a specific period of plant operation. Therefore, those streams may need to be sampled at a specified frequency in order to obtain a representative composite sample.

4.1.4 Other Sampling Point Considerations

In selecting sampling points for an environmental test, special considerations which may be involved in the final decision include:

- sampling practices of plant personnel,
- effect of sampling on process operation, and
- safety and work area requirements.

Most facilities have established sampling and analysis methods for routine process monitoring requirements. The sampling points and methods used by plant personnel should be evaluated with respect to the requirements of the particular test program. If these sampling points are acceptable, they should be used. Many times the sampling team can arrange to have plant personnel catch extra samples at their established sampling points, thus reducing the sampling effort.

Another consideration for sample point selection is the effect of the sampling effort upon the operation of the process itself. Sampling points must be selected so that entry into a stream will not adversely affect the process. This potential problem should be thoroughly discussed with plant personnel and if any danger of plant upset exists, operator approval should be obtained.

Safety and work area requirements are very important criteria for sampling point selection. The noise level, temperature, and atmospheric conditions to which the sampling team will be subjected must be considered. Additional considerations should include access to the sampling point, the availability of safe scaffolding or ladders and the availability of suitable means for transporting equipment to the sampling site. Problems associated with worker exposure to potentially hazardous materials must also be addressed.

4.2 SAMPLING METHOD SELECTION

The careful selection and execution of sampling procedures is the most critical step in producing reliable environmental test data. Samples must accurately represent the composition of the stream sampled and must be compatible with the analytical techniques to be applied. Factors which must be considered in order to maintain sample integrity and provide a representative sample include:

- stream composition as well as spatial and temporal variations in composition,
- potential for sample contamination and for changes in sample composition following its removal from the stream,

- sampling equipment reliability and size,
- possible limitations of the analytical techniques to be used, and
- the accuracy requirements of the test.

In addition, budget constraints will always be an important consideration.

Obtaining a small sample which is statistically representative of a much larger quantity of material (composite sample) is a common sampling problem. Spatial variations in composition can be averaged by compositing aliquots collected over the cross section of a flowing stream or throughout the volume of a static storage vessel or pile. However, it is best to avoid these variations by selecting a sampling location where the material is well mixed. Temporal variations can occur for a variety of reasons, ranging from stratification in a storage vessel to process operating fluctuations. They can be averaged by compositing aliquots collected over a period covering several process cycles or characterized in detail by analysis of each aliquot.

Samples may undergo changes in composition during sample collection (for example, vaporization of light organics from liquid samples or leaching of contaminants from the sampling equipment), periods of storage, or transport. Such changes must be minimized. For example, the loss of dissolved gases in a liquid sample may be prevented by collection and storage under pressure. Changes resulting from chemical reactions may be inhibited by storage at low temperatures or by designing chemical treatments specifically for the preservation of particular components. Unless a proven technique is available, time-stability studies to develop suitable preservation procedures or immediate on-site analysis should be considered.

The reliability of sampling equipment can impact the choice of sampling method. Generally, the more complex the equipment, the harder it is to maintain reliable operation for the duration of the sample collection period. In addition, as the sampling equipment increases in complexity, it generally increases in size. This may be a critical consideration if space is at a premium at the sampling location.

Sampling procedures may be grouped into two basic categories - manual (non-continuous) and automatic (continuous) sampling methods. Manual methods (*e.g.,* sampling trains) are generally more flexible, more easily executed, and more labor intensive than continous methods. Manual methods are often used as precursors to the installation of continuous monitors (on-line instrumentation) or for calibration of continuous sampling devices. Continuous techniques tend to be less flexible and more capital intensive than manual methods. Therefore, continuous techniques are usually preferred for long-term applications, whereas manual ones are often more appropriate for the short-term.

Presented in the Appendix is a detailed discussion of proven techniques for collecting representative samples from the three major stream types: gas, liquid, and solid. Sampling procedures for mixtures of these phases are addressed under the section dealing with each major phase. For example, sampling gases containing entrained particulate matter is discussed in the gas sampling section. Sampling liquid-solid slurries is discussed in the liquid sampling section.

4.3 SAMPLING FREQUENCY AND TIMING

Sampling frequency and timing are concerned with how often and when a sample should be collected. Sampling frequency (how often) is determined by the sampling method itself, the type of environmental test being performed, plant operational characteristics, quality control requirements, and data evaluation needs. Sampling timing (when) is concerned with insuring that the samples are collected under the desired plant operating conditions as defined by the test plan objectives.

4.3.1 Sampling Frequency

Sampling frequency may be method or process limited. Some sampling methods require several hours for collecting a suitable sample, such as obtaining a large sample of particulate matter in a gas stream having a low particulate loading. In such a case, sampling frequency may be limited to one sample per day. Other methods require only short collection times, such as collecting grab samples of a solid stream. These methods usually entail higher sampling frequencies and compositing techniques (see Appendix) if valid average samples are to be obtained.

There are two general types of processes (continuous and cyclic) that need to be discussed with respect to sampling frequency. For continous processes (*e.g.*, acid gas removal processes), the sampling time should be sufficiently long to average out normal process variations. Sampling cyclic or intermittent processes (*e.g.*, gasifier coal feed lock hoppers) can be approached in either of two ways:

- If the steps in the cycle are relatively long and well-defined, individual samples can be taken for each step.
- If the steps are short and undefined, sampling periods which span one or more cycles of operation can be used.

In some cyclic processes, there will be no input or output flows except at the beginning or end of the cycle. This would be the case for coal feed lock hoppers. In those cases, sample collection should take place only during flow conditions.

As previously indicated, the coal feed lock hopper is a good example of a cyclic process. In a Lurgi gasification plant, coal feed enters the gasifier through a lock hopper which cycles approximately every 12 minutes. Product gas is often used to pressurize the hopper before coal is fed into the gasifier. After the hopper is emptied, it is sealed and depressurized. The gas resulting from the depressurization step is the hopper outlet gas. Sampling the lock hopper might involve measuring key species in the pressurizing gas at the beginning of the cycle and measuring those same species in the outlet gas at the end of the cycle.

The sampling frequency can also be affected by the stipulations of the sampling quality control program (see Section 4.4) and by the data evaluation requirements (see Section 6.0). Sampling method limitations or plant operating characteristics may prevent full adherence to the sampling frequency specified in the test plan. If this occurs, deviations should be made with care such that the samples collected will still be representative of the streams and meet the test objectives.

4.3.2 Sampling Timing

The sampling timing (when to collect samples) is established primarily by the plant operation and the type of environmental test being performed. The plant operating conditions (normal operation, start-up, shutdown, emergency upsets) for the test will be specified by the test plan objectives. The following factors are important in defining the timing for sample collecting.

- For sampling at normal plant operating conditions, the plant should be given sufficient time to stabilize. Process data should be monitored to determine that these conditions are present. The engineering analysis of the plant should be used to define normal plant operation.
- For sampling during start-up, shutdown, and/or emergency upsets, sampling timing is critical and demands continuous or frequent sampling methods. The types of methods employed will depend upon the time required for start-up, shutdown, or the duration of the upset.

Sampling timing is most critical when determining the distribution of species or elements in process input and output streams (material balance tests). In material balance tests, the results of the engineering analysis of the process should be used to help define sampling timing. The engineering considerations include:

- residence time of the material in the process, and
- chemical reactions occurring in the process.

The residence time of the material in the process is dependent upon the flow characteristics of the material through the process. Knowledge of these flow characteristics allows estimates to be made of when the material or products of reactions involving the material will be present in the various process output streams.

A brief discussion of a sulfur balance around a coal gasifier will illustrate this concept. The residence time of a coal particle in a coal gasifier may be many hours. This includes the time required for the particle to enter the gasifier, react with steam and oxygen, and exit the gasifier (as ash). During most of this time interval, the coal particle will be continually undergoing devolatilization or gasification reactions. Therefore, sulfur species from the coal particle can contribute to the raw outlet gas sulfur species during the entire particle residence time.

In order to obtain a sulfur balance around the gasifier, several grab samples of inlet coal should be collected. The sulfur content in the outlet gas (including particulates, tars, and gaseous sulfur species) should be collected during the entire residence time interval. Several grab samples of ash should be collected before and after the calculated coal residence time in the gasifier. This time interval for collecting ash samples is necessary because of the possibility of channeling or recycle of coal particles inside the gasifier.

In summary, the engineering analysis of the plant should be used to define when to collect a sample in order to accomplish the test objectives. In many cases, judgments must be made on the time it takes a material to pass through a process (residence time) and when products of reactions will be present in the various process output streams.

4.4 SAMPLING QUALITY CONTROL PROGRAM

The purpose of a sampling quality control program is to prevent propagation of determinative errors (bias) through the sampling/analysis/evaluation phases of the test program. The specific items which should be addressed in a quality control program include:

- facilities and equipment inventory,
- training program,
- document control,
- quality control charts,

- supervision,
- materials inventory and procurement,
- reliability and maintenance,
- data validation,
- equipment calibration, and
- correlation tests.

Reasonable inventories of sampling and analytical accessories, spare parts, etc. should be maintained for the duration of the test. Periodic checks of the on- and off-site laboratories, sampling platforms, and data logging and processing areas should be performed to insure that they are in good condition.

Prior to the initiation of field work, all personnel involved in the test should be thoroughly briefed on the goals of the sampling and analysis program and the procedures to be followed including the use of special sample acquisition systems. All personnel should also be made aware of the need for instrument calibration, replicate samples, and other elements of quality control.

Provisions should be made to maintain complete security of sample log books, sampling and analytical data recording forms, and operating procedure documents to insure that data are not lost or mishandled. Duplicate record keeping is recommended along with specific procedures for distributing and making revision to documents affecting the quality control program.

Quality control charts should be used to track the day-to-day results of sampling and analytical efforts. The Shewhart Control Chart (Figure 4-3) is generally used for achieving this goal. Such a chart should be kept for duplicate analysis results, calibration constants, "spiked" sampling results (percent recovery), isokinetic sampling rates, and other factors which have a direct bearing on quality control. Normally, 3σ control limits are used, with 2σ being used as a warning limit. Sigma, σ, is the standard deviation of a set of two or more duplicate sample results.

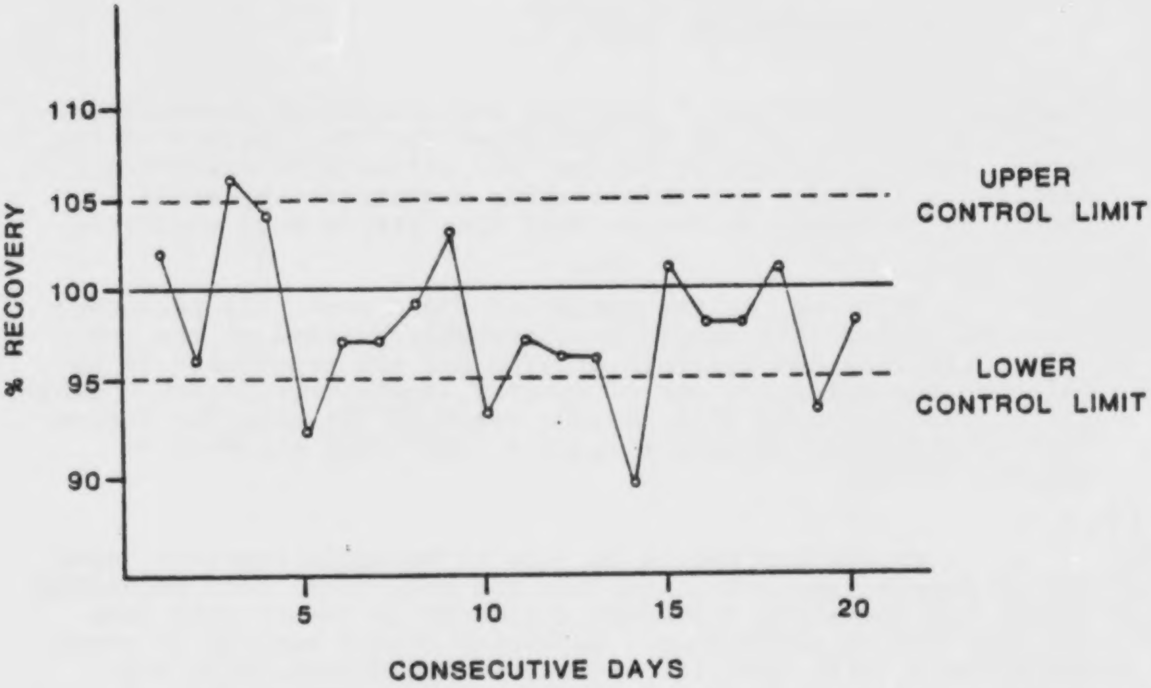


Figure 4-3. EXAMPLES OF A QUALITY CONTROL CHART FOR SPIKED SAMPLES (REF. 5).

Sampling personnel should routinely check the conformance of test team members to standard procedures for sampling, calibration, analysis, and data handling. Any deviations should be corrected immediately and an assessment of the effect of the deviation on results should be made. If necessary, tests should be repeated to ensure data validity.

Routine inventories of all reagents and supplies which are needed for quality control maintenance should be maintained. Purchasing guidelines should be established and documented so that delays in delivery will not affect data quality.

All measurement system components should be routinely serviced in accordance with manufacturer or developer recommendations. Reviewing equipment maintenance records prior to the time that the equipment is packed for shipment to the field is strongly recommended. The reliability of the equipment should routinely be checked to ensure that the maintenance procedures are adequate, and revisions should be made as needed to maintain data quality. Maintenance and reliability data should be recorded in log books.

Criteria for data validation should be stated in the test plan and revised as needed to maintain quality control. In the ideal case, data validation consists of two components:

- a routine set of both manual and computerized checks of measurement system performance at various points in the sampling/analysis/data processing sequence, and
- random audits of quality control performance by non-test team members. The quality control audit should check the test team adherence to standard procedures (a system review) and make independent quantitative checks as needed.

No quality control program can succeed unless all equipment is routinely calibrated by the use of appropriate standards. In addition, recovery tests for "spiked" samples should be a regular part of laboratory procedures, in order to check for chemical interferences (matrix effects). A quality control chart should be retained for recording recovery results.

Where possible, alternative sampling and analysis methods should be used to provide added assurance of data accuracy. Statistical correlation techniques can be used to ensure that the two methods are producing identical results, within experimental error.

The sampling strategy for an environmental test program needs to be thoroughly developed before the test is initiated. The sampling strategy should specify the actual locations of sample points, the methods for sample acquisition, the frequency and timing for sample collection, and the quality control program for obtaining representative samples such that with proper analysis techniques, the data will meet the objectives of the test.

SECTION 5.0

ANALYTICAL STRATEGY

An analytical strategy for an environmental test plan should define sample handling and preservation techniques along with specific analytical procedures required to accomplish the objectives of the test. Factors to be considered in selecting an analytical strategy include:

- compatibility with sampling procedures (amount of sample required and/or available),
- expected concentration levels and required detection limits,
- presence of interfering species,
- accuracy and precision requirements,
- requirements established by the quality control program, and
- time, equipment and cost limitations.

The selection and validation of analytical methods should be the responsibility of the analyst involved with the program. A number of alternate methodologies may be applied depending on available facilities and personnel. A selected list of analytical parameters of probable interest for environmental tests (waste stream, control equipment and process stream characterization) of a coal gasification facility is given in Table 5-1. Tables 5-2 and 5-3 list some specific organic species of potential concern. Table 5-4 outlines the protocol for the bioassay tests referred to in Table 5-1.

In the following sections, a discussion is presented of handling and preservation techniques for gas, liquid and solid samples followed by a discussion of the analytical methods for organic and inorganic analyses of those samples. Because

Table 5-1. ANALYTICAL PARAMETERS OF INTEREST FOR ENVIRONMENTAL TESTING OF COAL GASIFICATION FACILITIES

Solids	Liquids	Gases
Morphology	Physical Factors [e]	Particulate Matter[g]
Leachability Study[a]	Anions[f]	Major Components[h]
Ultimate Analysis (wt % of C, H_2, N_2, S, O_2)	Ammonia	Minor Components[i]
Proximate Analysis (wt % of moisture, ash volatile matter, fixed carbon)	Oil & Grease	Metal Carbonyls[j]
Trace Elements[b]	Phenols	Trace Elements[b]
Organic Species[c]	Trace Elements[b]	Organic Species[c]
Bioassay Tests[d]	Organic Species[c]	Bioassay Tests[d]
	Bioassay Tests[d]	

[a] Leachability studies: same analytical parameters as for liquids.

[b] Trace Elements: S, Al, Ca, Fe, Mg, K, Si, Na, P, Ti, Sb, As, Be, B, Cd, Cu, Cl, Cr, F, Pb, Li, Hg, Mn, Mo, Ni, Se, Ag, Tl, Sn, U, V, Zn

Actual trace elements analyzed will depend upon preliminary results from Sparks Source Mass Spectrometry Analysis.

[c] Organic Species: POM, PNA, BAP, Benzene, Nitrosamines, Phenols, Carboxylic Acids, and GC/MS analysis of nonpolar compounds, moderately polar compounds, polar neutral compounds, ethers of phenols, methyl esters of carboxylic acids, basic compounds, polar water soluble compounds, and very polar water soluble compounds. Tables 5-2 and 5-3 list specific organic species of potential concern.

The extent of organic characterization will depend upon preliminary organic screening tests and the amount of organics present in a sample.

[d] Bioassay Tests: Table 5-4 gives the bioassay tests for solid, liquid, and gas samples.

[e] Physical Factors: pH, temperature, specific conductance, TSS, TDS, hardness, acidity, alkalinity, COD, BOD, TOC

[f] Anions: Chloride, Fluoride, Sulfate, Sulfite, Sulfide, Nitrate, Phosphate, Cyanide.

[g] Particulate Matter: Same analytical parameters as for solids.

[h] Major Components: CO, CO_2, N_2, H_2, O_2.

[i] Minor Components: HCN, H_2S, COS, CS_2, SO_2, Mercaptans, Thiophenes, NH_3, NO_x.

[j] Metal Carbonyls: $Fe(CO)_5$, $Ni(CO)_4$.

Table 5-2. ENVIRONMENTALLY HAZARDOUS ORGANIC SPECIES POTENTIALLY PRESENT IN COAL GASIFICATION FACILITY PROCESS AND WASTE STREAMS

Compound	Hazard
POLYCYLCIC AROMATICS	
Naphthalenes	
Nephthalene	Suspected carcinogen
1-Methyl naphthalene	Toxic
Acenaphthenes	
Acenaphthene	Suspected carcinogen
Anthracenes	
Anthracene	Suspected carcinogen
9-Methylanthracene	Suspected carcinogen
Phenanthrenes	
Penanthrene	Toxic
Pyrenes	
Pyrene	Carcinogen
Fluoranthenes	
3-Methylfluoranthene	Suspected carcinogen
Fluoranthene	Toxic
Indenopyrenes	
Indeno (1,2,3-c,d)pyrene	Suspected carcinogen
Cholanthrenes	
Cholanthrene	Suspected carcinogen
3-Methylcholanthrene	Suspected carcinogen
Chrysenes	
Chrysene	Carcinogen
5,6-Demethylchrysene	Suspected carcinogen
5-Methylchrysene	Carcinogen
Benzanthracenes	
Benz(a)anthracene	Carcinogen
6,8-Dimethylbenz(a)anthracene	Suspected carcinogen
7,12-Dimethybenz(a)anthracene	Suspected carcinogen
8,12-Dimethylbenz(a)anthracene	Suspected carcinogen
1-Methylbenz(a)anthracene	Suspected carcinogen
2-Methylbenz(a)anthracene	Suspected carcinogen
Benzophenanthrenes	
Benzo(c)phenanthrene	Carcinogen
2-Methylbenzo(c)phenanthrene	Suspected carcinogen
Benzofluoranthenes	
Benzo(j)fluoranthene	Carcinogen
Benzo(b)fluoranthene	Carcinogen
Benzo(k)fluoranthene	Suspected carcinogen
Benzopyrenes	
Benzo(a)pyrene	Carcinogen
Benzo(e)pyrene	Carcinogen
3-Methylbenzo(a)pyrene	Suspected carcinogen
Perylenes	
Perylene	Suspected carcinogen
Dibenzanthracenes	
Dibenz(a,H)anthracene	Carcinogen
Dibenz(a,c)anthracene	Suspected carcinogen
Dibenz(a,j)anthracene	Suspected carcinogen
Dibenzopyrenes	
Dibenzo(a,i)pyrene	Carcinogen
Dibenzo(a,d)pyrene	Suspected carcinogen
Dibenzo(a,e)pyrene	Suspected carcinogen
5-Methyldibenzo(a,l)pyrene	Suspected carcinogen
Benzoperylenes	
Benzo(ghi)perylene	Carcinogen
Dibenzopentaphenes	
Dibenzo(h,rst)pentaphene	Suspected carcinogen
Dibenzoperylenes	
Peropyrene	Suspected carcinogen
NITROGEN HETEROCYCLICS	
Pyrroles	
Pyrrole	Toxic
Morpholines	
Morpholine	Irritant
N-Ethylmorpholine	Irritant
Bismorpholinomethane	Carcinogen
Pyridines	
Pyridine	Irritant
a-Picoline	Irritant
3,4-Dihydroxypyridine	Carcinogen
Indoles	
Indole	Suspected carcinogen
Carbazoles	
Carbazole	Toxic
Benzocarbazoles	
Benzo(a)carbazole	Suspected carcinogen
Dibenzocarbazoles	
7H-Dibenzo(c,g)carbazole	Carcinogen
7H-Dibenzo(a,i)carbazole	Suspected carcinogen
7H-Dibenzo(a,g)carbazole	Suspected carcinogen
Quinolines	
Quinoline	Toxic
Isoquinoline	Toxic

Continued

Table 5-2. (Continued) ENVIRONMENTALLY HAZARDOUS ORGANIC SPECIES POTENTIALLY PRESENT IN COAL GASIFICATION FACILITY PROCESS AND WASTE STREAMS

Page 2

Compound	Hazard
Benzacrindines	
Benz(c)acridine	Suspected carcinogen
7,9-Dimethylbenz(c)acridine	Suspected carcinogen
7-Methylbenz(c)acridine	Carcinogen
Dibenzacridines	
Dibenz(a,J)acridine	Carcinogen
Diben(a,h)acridine	Carcinogen
Phenazines	
Phenazine	Suspected carcinogen
NON-HETEROCYCLIC NITROGEN COMPOUNDS	
Nitriles	
Acetonitrile	Toxic
Acrylonitrile	Toxic
Aliphatic Amines	
Piperidine	Toxic
Methylamine	Irritant
Ethylamine	Irritant
n-Propylamine	Irritant
n_Butylamine	Irritant
Triethylamine	Irritant
Ethylenediamine	Irritant
Cyclohexylamine	Irritant
Dicyclohexylamine	Irritant
Dimethylamine	Mutagenic
Allylamine	Irritant
Amides	
Acrylamide	Toxic
Acetamide	Carcinogen
N,N-Diethylacetamide	Suspected carcinogen
Acetylaminofluoranthene	Suspected carcinogen
Thioacetamide	Mutagenic
Acetanilide	Mutagenic
Aromatic Amines	
o-Toluidine	Suspected carcinogen
m-Toluidine	Suspected carcinogen
B-Naphthylamine	Carcinogen
Diphenylamine	Suspected carcinogen
Benzidine	Suspected carcinogen
4-Amino-biphenyl	Suspected carcinogen
Aniline	Toxic
4,4-Methylenedianiline	Suspected carcinogen
Aminoazobenzene	Suspected carcinogen
Benzylamine	Irritant
p-Phenylenediamine	Irritant
Imines	
Ethylenimine	Toxic
Hydroxylamines	
N-Hydroxyaniline	Mutagenic
N-2-Naphthylhydroxylamine	Suspected carcinogen
Hydroxylamine	Mutagenic
Hydrazines	
Hydrazine	Suspected carcinogen
1,3-Diethylhydrazine	Suspected carcinogen
Methylhydrazine	Suspected carcinogen
Hydroazobenzene	Suspected carcinogen
Semicarbazides	
Semicarbazide	Carcinogen
Azo Compounds	
Azobenzene	Suspected carcinogen
Azoethene	Suspected carcinogen
SULFUR COMPOUNDS	
Thioureas	
Thiourea	Suspected carcinogen
Mercaptans, Aliphatic	
Methylmercaptan	Disagreeable odor
Ethylmercaptan	Disagreeable odor
Isopropylmercaptan	Disagreeable odor
n-Propylmercaptan	Disagreeable odor
2-Pentylmercaptan	Disagreeable odor
Isoamylmercaptan	Disagreeable odor
n-Amylercaptan	Disagreeable odor
n-Hexylmercaptan	Disagreeable odor
3-Mercaptoethanol	Mutagenic
Mercaptans, Aromatic	
Thiophenol	Disagreeable odor
Benzylmercaptan	Disagreeable odor
p-Thiocresol	Disagreeable odor
Thioraphthol	Disagreeable odor
Sulfonic Acids	
Benzenesulfonic acid	Irritant
Methanesulfonic acid	Irritant
Sulfuric Acid Esters	
Dimethylsulfate	Suspected carcinogen
n-Propylmethanesulfonate	Mutagenic
Sulfoxides	
Dimethylsulfoxide (DMSO)	Suspected carcinogen
Sulfides	
Carbon disulfide	
Thiophenes	
Thiophene	
BENZENE DERIVATIVES	
Polyaryls	
Biphenyl	Toxic

Continued

Table 5-2. (Continued) ENVIRONMENTALLY HAZARDOUS ORGANIC SPECIES POTENTIALLY PRESENT IN COAL GASIFICATION FACILITY PROCESS AND WASTE STREAMS

Page 3

Compound	Hazard
Double Bond Conjugated Benzenes	
Styrene	Toxic
Alkylbenzenes*	
Benzene	Suspected carcinogen
PHENOLS	
Phenol	Suspected carcinogen
b-Chlorophenol	Suspected carcinogen
2,4-Xylenol	Suspected carcinogen
2,5-Xylenol	Suspected carcinogen
2,6-Xylenol	Suspected carcinogen
3,4-Xylenol	Suspected carcinogen
3,5-Xylenol	Suspected carcinogen
o-Cresol	Toxic
m-Cresol	Toxic
p-Cresol	Toxic
1-Naphthol	Toxic
2-Naphthol	Toxic
Pyrogallol	Irritant
Hydroquinone	Irritant
CARBOXYLIC ACIDS	
Aliphatic Acids	
Formic Acid	Caustic
Acetic Acid	Caustic
Propionic Acid	Disagreeable odor
Butyric Acid	Disagreeable odor
Valeric Acid	Disagreeable odor
Caproic Acid	Disagreeable odor
Acrylic Acids	
Acrylic Acid	Irritant
Methacrylic Acid	Irritant
Carbamates	
Methylcarbamate	Mutagenic
Ethylcarbamate	Mutagenic
n-Butylcarbamate	Mutagenic
n-Propylcarbamate	Mutagenic
Lactones	
B-Propiolactone	Mutagenic
v-Butyrolactone	Mutagenic
Amino Benzoic Acids	
Anthranilic Acid	Suspected carcinogen
Aliphatic Aldehydes	
Formaldehyde	Irritant
Acetaldehyde	Suspected carcinogen
Propionaldehyde	Irritant
Butyraldehyde	Irritant
Hyceraldehyde	Mutagenic
Aliphatic Ketones	
Acetone	Irritant
Methylethylketone	Irritant
Cyclohexanone	Carcinogen
a.3 Unsaturated Carbonyls	
Acrolein	Irritant
Crotonaldehyde	Irritant
Aromatic Carbonyls	
Acetophenone	Irritant
Furfural	Irritant
Quinones	
Benzoquinone	Suspected carcinogen
Anthraquinone	Suspected carcinogen
2-Methylbenzoquinone	Suspected carcinogen
OTHER SPECIES	
Oxygen Heterocyclics	
p-Dioxane	Suspected carcinogen
Coumarin	Suspected carcinogen
Alcohols	
Methanol	Toxic
Ethanol	Suspected carcinogen
Allyl alcohol	Irritant
Ethylene Glycol	Suspected carcinogen
Cyclohexanol Carcinogenic	
Gaseous Species	
Hydrogen Cyanide	Toxic
Carbonyl Sulfide	Toxic
Carbon Monoxide	Toxic
1,3 Butadiene	Irritant

---

*Other major alkylbenzenes present as major constituents of their class are also significant.

Table 5-3. ORGANIC SPECIES FROM EPA EFFLUENT GUIDELINES (Ref. 6)

1,3-Dichlorobenzene
1,4-Dichlorobenzene
Hexachloroethane
1,2-Dichlorobenzene
bis(2-Chloroisopropyl)ether
Hexachlorobutadiene
1,2,4-Trichlorobenzene
Naphthalene
Nitrobenzene
bis(2-Chloroethyl)ether
bis(2-Chloroethyoxy)methane
Hexachlorocyclopentadiene
2-Chloronaphthalene
Acenaphthylene
Acenaphthene
Isophorone
Fluorene
2,6-Dinitrotoluene
2,4-Dinitrotoluene
4-Chlorophenyl phenyl ether
Diphenylhydrazine
Dimethyl phthalate
N-nitrosodiphenylamine
Hexachlorobenzene
4-Bromophenyl phenyl ether
Diethylphthalate
Phenanthrene/Anthracene
d$_{10}$-Anthracene
Di-n-butylphthalate
Fluoranthene
Pyrene
Benzidine
Butyl benzyl phthalate
Chrysene/Benzo(a)anthracene
bis(2-Ethylhexyl)phthalate
Benzo(b)fluoranthene/ Benzo(a)pyrene
Indeno(1,2,3-c,d)pyrene
Dibenzo(a,h)pyrene
Benzo(g,h,i)perylene
N-nitrosodimethylamine
N-nitrosodi-n-propylamine
Endrin aldehyde
Endosulfan sulfate
3,3'-Dichlorobenzidine
2,3,7,8-TCDD
Chloromethane
Dichlorodifluoromethane
Bromomethane
Vinyl chloride
Chloroethane
Methylene chloride
Trichlorofluoromethane
1,1-Dichloroethylene
Bromochloromethane (IS)
1,1-Dichloroethane
Trans-1,2-dichloroethylene
Chloroform
1,2-Dichloroethane
1,1,1-Trichloroethane
Carbon tetrachloride
Bromodichloromethane
bis(chloromethyl)ether
1,2-Dichloropropane
Trans-1,3-dichloropropene
Trichloroethylene
Dibromochloromethane
1,1,2-Trichloroethane
cis-1,3-Dichloropropene
Benzene
2-Chloroethyl vinyl ether
2-Bromo-1-chloropropane (IS)
Bromoform
1,1,2,2-Tetrachloroethane
1,4-Dichlorobutane (IS)
1,1,2,2-Tetrachloroethene
Toluene
Chlorobenzene
Ethylbenzene
Phenol
2-Chlorophenol
2-4-Dimethylphenol
2-Nitrophenol
2,4-Dichlorophenol
p-Chloro-m-cresol
2,4,4-Trichlorophenol
2,4-Dinitrophenol
4-Nitrophenol
4,6-Dinitro-o-cresol
Pentachlorophenol
d$_{10}$-Anthracene (IS)

Table 5-4. BIOASSAY PROTOCOL FOR SOLID, LIQUID AND GAS SAMPLES (Ref. 1)

Sample	Health Effects		Ecology Effects		
Water/Liquids	Microbial Mutagenesis	Rodent Acute Toxicity	Algal Bioassay	Static Bioassay	Soil Microcosm
Solids	Microbial Mutagenesis	Rodent Acute Toxicity	Algal Bioassay	Static Bioassay	Soil Microcosm
Gases					Plant Stress Ethylene
Particulates	Microbial Mutagenesis	Rodent Acute Toxicity (Cytotoxicity)			Soil Microcosm
Sorbent (XAD-2)	Microbial Mutagenesis	Cytotoxicity			

of the large number of analytical methods discussed in this section, they are presented according to the parameter to be analyzed. A brief summary of the specific methods and a list of references where detailed discussions of the methods can be found are presented.

5.1 SAMPLE HANDLING AND PRESERVATION

After samples have been obtained from various streams in the process, they should be prepared for analysis and/or storage. The bulk samples from each sampling point should be taken to some central location equipped to perform the preservation and treatment procedures, probably a stationary or mobile laboratory facility. The handling and preservation requirements for the analytical parameters of interest in each stream should be integrated into a total sampling/preservation/analytical scheme for greatest efficiency. The requirements of such a scheme will determine the number of individual aliquots into which the bulk sample is divided. Some level of sample division may have already occurred as part of the sampling techniques. For many of the parameters of interest, preservation will allow the sample to be transported to off-site facilities for analysis. Others will require immediate, on-site analysis due to their instability.

5.2 ANALYTICAL TECHNIQUES

In this section the analytical techniques for analyzing samples collected from coal gasification facilities are summarized. A detailed description of each technique is not included here. Instead, references are given so that the reader may readily obtain detailed descriptions of each technique. Again, it should be emphasized that the selection of analytical techniques depends upon the following factors:

- compatibility with the sample procedures,
- expected concentrations and detection limits,
- presence of interfering species,
- accuracy and precision requirements,

- requirements established by the quality control program, and
- time, equipment and cost limitations.

In the following sections analytical methods are divided into screening (qualitative) and quantitative techniques. In each of these divisions, analytical methods for inorganic and organic analyses are presented separately. Biological tests are discussed only in the section dealing with screening techniques.

5.2.1 Analytical Screening Techniques

In this section, analytical screening techniques for environmental tests are discussed. These techniques, which are used for Level 1 waste stream characterization tests, are specified in the IERL-RTP Procedures Manual: Level 1 Environment Assessment (Ref. 1).

Inorganic Analysis -

The Level 1 (screening) procedures for inorganic analyses in solid, liquid, and gas streams are given in Table 5-5. For most trace element analyses, spark source mass spectrometry (SSMS) is used. Exceptions to this are mercury, antimony, and arsenic. The sample type, preparation and analysis procedures for SSMS and for mercury, antimony, and arsenic analyses are outlined in Figure 5-1 and 5-2, respectively.

Reagent test kits are used for the other inorganic components shown in Table 5-5. These analyses are primarily for liquid samples (including leachates). The analytical techniques used for each of these components are given in Section 5.2.2.

Organic Analysis -

Level 1 screening procedures for analyzing organics in gaseous, liquid, and solid waste streams are shown in Figure 5-3. Gases and organic liquids (including extracts) are analyzed by gas chromatography for C_1-C_6 hydrocarbons. Liquids and extracts are further examined by infrared (IR) spectrometry for the

Table 5-5. ANALYTICAL PARAMETERS FOR SCREENING INORGANIC CONSTITUENTS IN SOLID, LIQUID, AND GAS SAMPLES

Sample Type	Analytical Parameters	Analytical Technique[a]
Solid	Trace Elements	SSMS
Gas	Trace Elements	SSMS
Liquid (including leachates)	Trace Elements Water Quality Parameters[b]	SSMS (See Table 5.8 in Section 5.2.2)
Particulate Matter	Trace Elements Morphology	SSMS Ref. 1

[a] Detailed discussion of the analytical techniques for these analytical parameters are given in the Level 1 environmental assessment manual (Ref. 1).

[b] Water quality parameters: acidity, alkalinity, pH, COD, BOD, TOC, conductivity, TDS, TSS, dissolved oxygen, ammonia, cyanide, sulfate, sulfite, sulfide, nitrate, nitrite, carbonate, and thiocyanate.

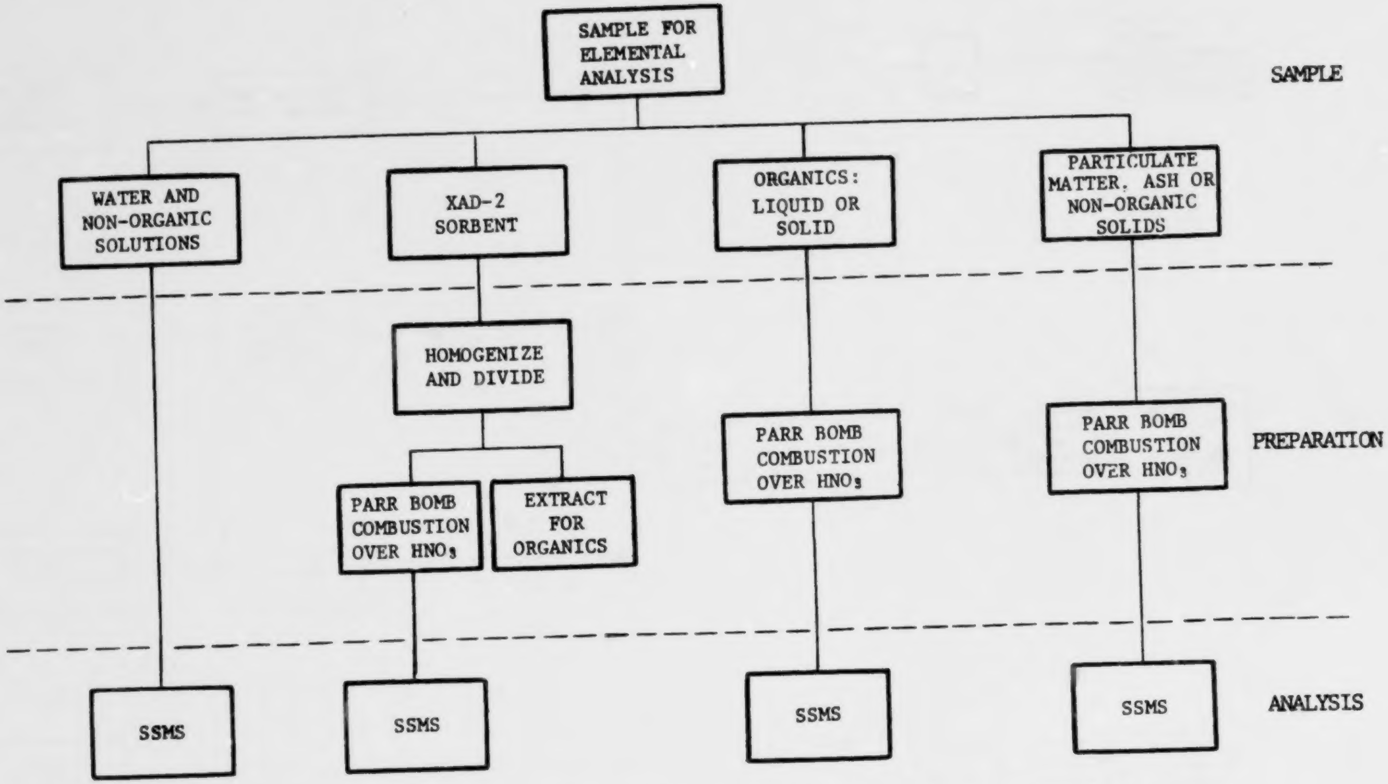

SAMPLE FOR ELEMENTAL ANALYSIS
SAMPLE
WATER AND NON-ORGANIC SOLUTIONS
XAD-2 SORBENT
ORGANICS: LIQUID OR SOLID
PARTICULATE MATTER, ASH OR NON-ORGANIC SOLIDS
HOMOGENIZE AND DIVIDE
PARR BOMB COMBUSTION OVER HNO₃
EXTRACT FOR ORGANICS
PARR BOMB COMBUSTION OVER HNO₃
PARR BOMB COMBUSTION OVER HNO₃
PREPARATION
SSMS
SSMS
SSMS
SSMS
ANALYSIS

Figure 5-1. OUTLINE OF LEVEL L ELEMENTAL ANALYSES USING SPARK SOURCE MASS SPECTROMETRY (SSMS)

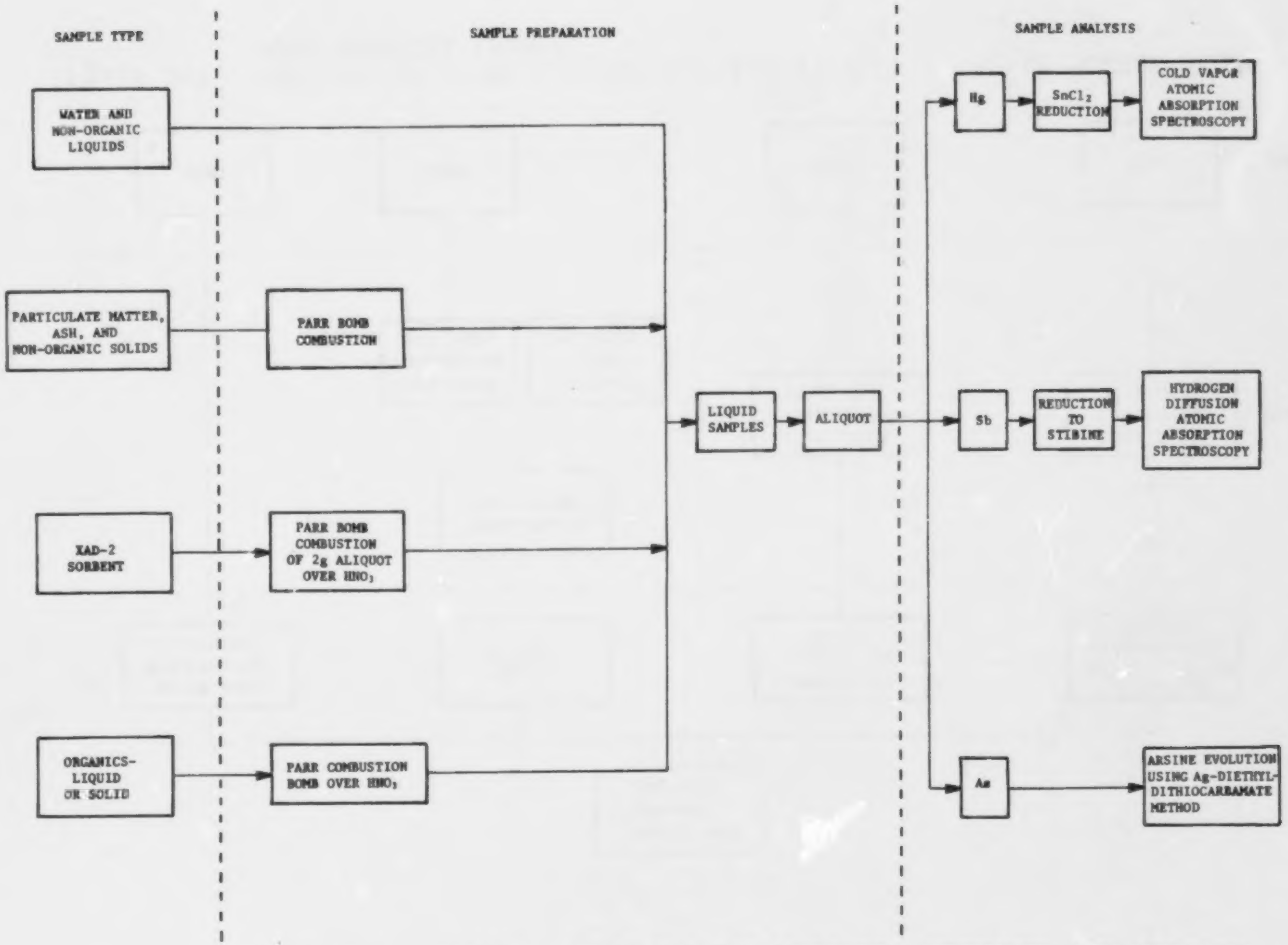
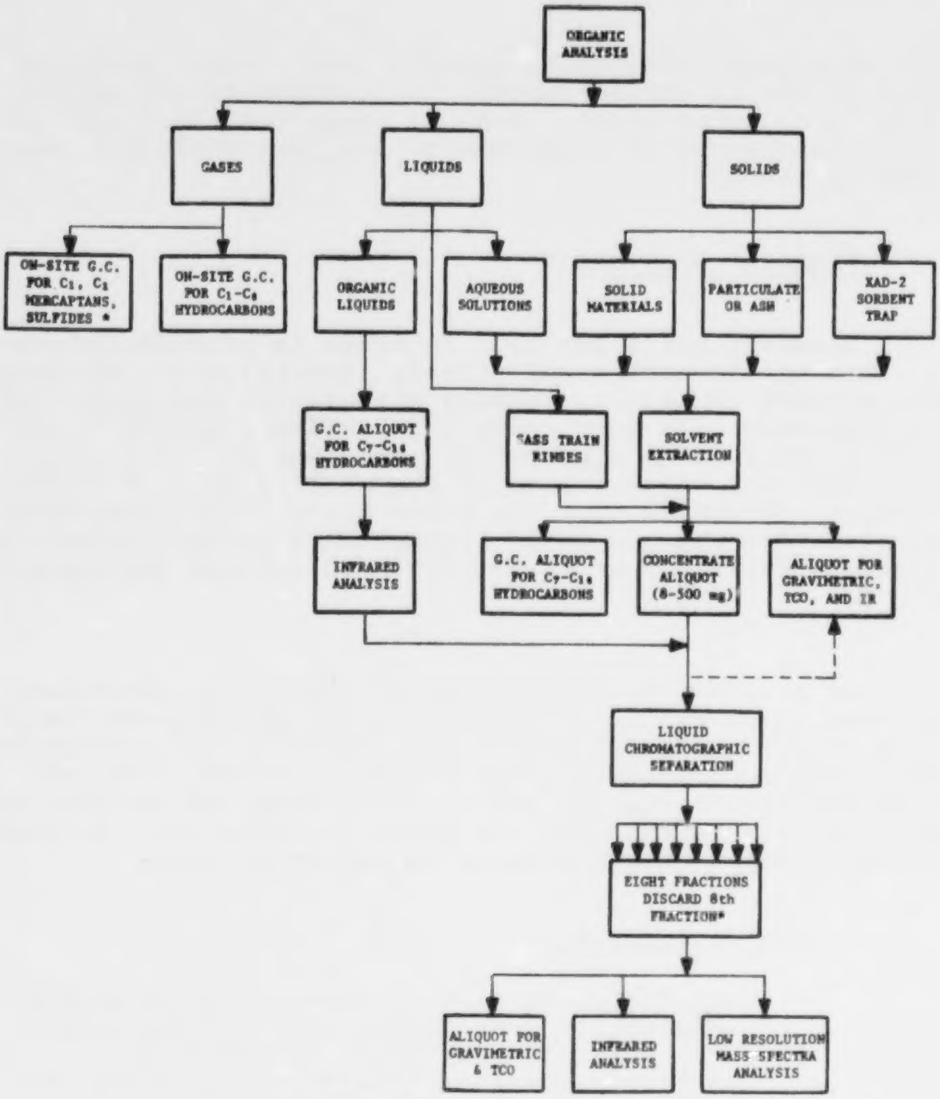

SAMPLE TYPE
SAMPLE PREPARATION
SAMPLE ANALYSIS
WATER AND NON-ORGANIC LIQUIDS
PARTICULATE MATTER, ASH, AND NON-ORGANIC SOLIDS
XAD-2 SORBENT
ORGANICS-LIQUID OR SOLID
PARR BOMB COMBUSTION
PARR BOMB COMBUSTION OF 2g ALIQUOT OVER HNO3
PARR COMBUSTION BOMB OVER HNO3
LIQUID SAMPLES
ALIQUOT
Hg
SnCl2 REDUCTION
COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY
Sb
REDUCTION TO STIBINE
HYDROGEN DIFFUSION ATOMIC ABSORPTION SPECTROSCOPY
As
ARSINE EVOLUTION USING Ag-DIETHYL-DITHIOCARBAMATE METHOD

Figure 5-2. LEVEL 1 ANALYSES FOR MERCURY, ANTIMONY AND ARSENIC


ORGANIC ANALYSIS
GASES
LIQUIDS
SOLIDS
ON-SITE G.C. FOR C_1, C_2 MERCAPTANS, SULFIDES *
ON-SITE G.C. FOR C_1-C_6 HYDROCARBONS
ORGANIC LIQUIDS
AQUEOUS SOLUTIONS
SOLID MATERIALS
PARTICULATE OR ASH
XAD-2 SORBENT TRAP
G.C. ALIQUOT FOR C_7-C_{16} HYDROCARBONS
SASS TRAIN RINSES
SOLVENT EXTRACTION
INFRARED ANALYSIS
G.C. ALIQUOT FOR C_7-C_{16} HYDROCARBONS
CONCENTRATE ALIQUOT (8-500 mg)
ALIQUOT FOR GRAVIMETRIC, TCO, AND IR
LIQUID CHROMATOGRAPHIC SEPARATION
EIGHT FRACTIONS DISCARD 8th FRACTION*
ALIQUOT FOR GRAVIMETRIC & TCO
INFRARED ANALYSIS
LOW RESOLUTION MASS SPECTRA ANALYSIS

*Recommended procedure, but not officially part of Level 1 analysis.

Figure 5-3. OUTLINE OF LEVEL 1 ORGANIC ANALYSES

presence of organic functional groups. The liquids are then subjected to liquid chromatography to fractionate the sample according to compound class. Each of these fractions are subsequently analyzed by IR spectrometry and low resolution mass spectrometry (LRMS).

Bioassay Analysis -

Bioassay tests are used in order to provide information concerning the biological effects (synergism vs. antagonism) of waste streams containing complex mixtures of inorganic and organic compounds. In most cases those effects cannot be projected from the results of physical and chemical tests alone. Bioassay tests may be performed on the whole sample or fractions of the sample depending upon the waste stream characteristics. For example, if a gaseous waste stream contains particulate matter, bioassay tests may be needed for both the gas and particulates.

At present, specific bioassay analytical procedures are not completely defined. However, types of bioassay tests are being studied to assess their applicability for evaluating the health and ecological effects of waste streams from coal gasification facilities. These tests, their expected results and the amount of sample required are given in Table 5-6. A brief discussion of these bioassay tests is presented below:

- Health Effects
  - Ames Test: is used to measure the potential mutagenicity (carcinogenicity) of the sample. Three histidine deficient Sallmonella Typhimurim strains (TA-1535, TA-1537 and TA-1538) are used. The reversion of the strains to prototrophy indicates mutation (Ref. 7, 8, and 9).
  - Cytotoxicity Test: is used to estimate the acute cellular toxicity of a sample from an in-vitro cell mortality test using rabbit lung aveolar macrophages. The results of this test are extrapolated to obtain an EC_{50} value for the sample.

Table 5-6. BIOASSAY PROTOCOL FOR LEVEL 1 WASTE STREAM CHARACTERIZATION TESTS[a]

Bioassay Tests (Classification of Sample to be Tested: Solid, Liquid, Gas)	Results of the Test[b]	Amount of Sample Tested
Health Tests (Solid, Liquid)		
Ames	+1-	1 g
Cytotoxicity	+1-, EC$_{50}$	1/2 g
WI-38	+1-, EC$_{50}$	1/2 g
Rodent Acute Toxicity	+1-, LD$_{50}$	50 g
Ecological Tests (Solid, Liquid)		
Freshwater		
• Algal	+1-, EC$_{50}$	50 ℓ
• Daphnia	+1-, LC$_{50}$	50 ℓ
• Fish	+1-, LC$_{50}$	50 ℓ
Saltwater		
• Algal	+1-, EC$_{50}$	50 ℓ
• Shrimp	+1-, LC$_{50}$	50 ℓ
• Fish	+1-, LC$_{50}$	50 ℓ
Terrestrial		
• Soil microcosm	+1-, Ranking	10 g
• Plant stress ethylene (gas sample only)	+1-	1360 ℓ

---

[a] The exact procedures for each of these bioassay tests are currently being developed by the EPA.

[b] +1-: toxic/nontoxic; EC$_{50}$ and LC$_{50}$: concentration required to kill 50% of the biological species tested; LD$_{50}$: dose required to kill 50% of the species tested.

  - WI-38 Test: is used to estimate the acute cellular toxicity of a sample from an in-vitro WI-38 cell mortality test. As in the cytotoxicity test, the results are extrapolated to obtain an EC_{50} for the sample.

  - Rodent Acute Toxicity Test: is used to measure the acute toxicity of a sample in a whole animal. The test is performed by administering known levels of the sample to a small population of mice and extrapolating the mortality rate to obtain an LC_{50} value. Other effects on the mice, such as loss of hair, bleeding at the nose, etc., should also be recorded during the test.

- Ecological Effects

  - Freshwater Tests: are used to estimate the acute toxicity of a sample by exposing selected aquatic species (algae, daphnia and fathead minnows) to several levels of sample concentrations. An EC_{50}, for algae, and an LC_{50}, for daphnia and minnows, are obtained by extrapolation.

  - Saltwater Tests: are used to estimate the acute toxicity of a sample by exposing selected species (algae, mysid shrimp and sheepshead minnows) to various concentrations of sample. An EC_{50} and LC_{50}'s are estimated from the algal test and the shrimp and minnow tests, respectively.

  - Plant Stress Ethylene Test: is used to estimate the effects of gaseous waste streams on five-week-old soybean plants. Variations in the amounts of ethylene produced by the plants are measured for various exposure times and gas volumes. The results of this test indicate whether the sample was toxic (increase in ethylene production) or nontoxic (no change in ethylene production).

  - Soil Microcosm Test: is used to measure the variations in oxygen consumption and carbon dioxide production of soil samples containing microorganisms. The results from this test give a toxic/nontoxic result along with a severity ranking of each sample tested.

In summary, screening analytical techniques are effective in determining whether a stream or portions of the stream need further chemical or biological characterization. Procedures for quantitative chemical analysis of environmentally significant streams are presented in the following section. Quantitative biological tests have not been defined by the EPA.

5.2.2 Quantitative Analytical Procedures

Quantitative analytical techniques for characterizing chemical species in waste and process streams are discussed in this section. These techniques are used for Level 2 and 3 waste stream characterization tests and for control equipment and process stream characterization tests. In the following text, a summary of quantitative techniques for analyzing inorganic and organic species in gas, liquid, and solid samples is presented. A detailed description of each of these procedures is not included; however, references are given to indicate where a detailed discussion can be found.

Inorganic Analysis -

Inorganic species of interest in environmental tests for coal gasification facilities are given in Table 5-1. Inorganic analysis generally consists of two steps: 1) sample preparation, and 2) species identification and/or quantification. Preparation techniques for gas, liquid, and solid samples are discussed below. Analytical methods for identifying and quantifying inorganics in those samples are then presented.

Sample Preparation - In most cases gaseous, liquid and solid samples require preparation prior to analysis for inorganic species. These preparation techniques are summarized in the following text. A more detailed discussion is contained in a report by Richard Luthy, "Manual of Methods: Preservation and Analysis of Coal Gasification Wastewaters" (Ref. 10).

The gas samples collected in impinger solutions require preparation procedures similar to those for liquid samples being analyzed for analogous species (*e.g.*, NH_3 and HCN are analogous to NH_4^+ and CN^-). Sulfur species in impinger solutions (COS, H_2S, CS_2 and SO_2) are oxidized with hydrogen peroxide for analysis as sulfate. Condensable organics collected in impingers may require extraction or dissolution of an immiscible organic phase prior to analysis.

Vapor phase trace elements collected by wet electrostatic precipitator (WEP) sampling (described in the Appendix) require that particulates suspended in the electrolyte solution be filtered, digested, and the digested solution added back to the electrolyte solution prior to analysis.

Gas grab samples may require pretreatment (*e.g.*, drying and filtering) prior to analysis by gas chromatography or other instrumental techniques. Great caution must be exercised to insure that the gas species of interest are not lost or changed in pretreatment. Another area of precaution involves the probability of certain gaseous species sorbing on or reacting with the walls of the gas collection container (glass bomb or bag). Pretreatment of the collection container with a gas containing the gas species of interest may be required. However, the possibility of desorption of the pretreatment species from the container walls into the sample gas must also be avoided.

Some liquid samples may require distillation or acid digestion prior to analysis to exclude interfering species or to stabilize the compound of interest. Examples of inorganic species that require distillation pretreatment include cyanide, fluoride and ammonia. Analyses for trace elements usually require acid digestion to oxidize the elements present to a stable valence state (Ref. 11).

Organic liquids, such as tars and oils, may require dilution with a solvent to facilitate sample handling. Trace element analysis requires a high temperature and pressure acid digestion technique (Ref. 12) using a sealed metal bomb with a Teflon insert.

The first step in preparing solid samples is to insure homogeneity. This can be accomplished by mixing and grinding the sample to less than 200 mesh. Drying the sample is often required with concurrent gravimetric determination of moisture content. The drying temperature must be selected to avoid loss of volatile compounds. For samples with a high moisture content, drying may be necessary to allow mixing, grinding and sizing.

Identification and Quantification Procedures - Once the samples are in a form compatible with the analytical technique, the species of interest can be identified and/or quantified. The extent of this determination can range from the identification of classes or groups of species to the accurate quanitification of specific compounds.

Analytical procedures which have been proven effective in analyzing for the inorganic species listed in Table 5-1 are summarized in Tables 5-7 through 5-9.

These tables list the species to be analyzed, the amount of sample required, the sample container, how the sample is collected, the maximum holding time allowable before analysis, the sample preparation required and a general description of the analytical technique along with references. General reference sources for inorganic analysis include:

- Standard Methods, 14th edition (Ref. 13),
- 1977 Annual Book of ASTM Standards - Part 31 - Water (Ref. 14),
- Manual of Methods for Chemical Analysis of Water and Wastes, 1974, EPA (Ref. 11),
- Assessment, Selection, and Development of Procedures for Determining the Environmental Acceptability of Synthetic Fuels Plants Based On Coal, (Ref. 15),
- Detection and Determination of Trace Elements, 6th Edition, Maurice Pinta (Ref. 16), and
- Quantitative Analysis of Gaseous Pollutants, Ruch, (Ref. 17).

An example of an integrated scheme for inorganic analysis of liquid samples from a coal gasification facility is

Table 5-7. INORGANIC ANALYTICAL METHODS FOR COAL GASIFICATION PROCESSES (GASEOUS)

Gases	Sample Quantity Requirements	Container[1]	Collection System	Holding Time	Preparation	Analytical Method, Reference
Grab Samples:						
CO, CO_2, N_2, H_2, O_2	1 liter each	Scotchpack	Grab Sample	(on-site analysis)	Drying	Gas Chromatography, Ref. 1, 18, 19, 20
H_2S, CS_2, COS, SO_2	1 liter each	Glass Bomb	Grab Sample	(on-site analysis)	Drying	Gas Chromatography, Ref. 1, 18, 19, 20
NO_x	1 liter	Tedlar bag	Grab Sample	(on-site analysis)	Drying	Chemiluminescence, commercial instrumentation, Ref. 21
Ammonia	250 mls	P, G	Impinger Collection in 10% H_2SO_4	Cool, 4°C, 24 hours	Distillation	Titrimetric, Ref. 11, 13, 14
Cyanide	250 mls	P, G	Impinger Collection in 10% NaOH	Cool, 4°C, 24 hours	Distillation	Spectrophotometric, Ref. 11, 13, 14
Sulfur Species:						
H_2S	250 mls	P, G	Impinger Collection in basic Zn acetate	Cool, 4°C, 24 hours	Precipitation, filtration, dissolution	Titrimetric, Ref. 9, 13
SO_2	250 mls	P, G	H_2O_2 impinger	Cool, 4°C, 7 days	None	Turbidimetric, SO_4, Ref. 11, 13, 14
Total Sulfur (H_2S, COS, CS_2, SO_2)	250 mls	P, G	Impinger Collection in: 1st: Iodine 2nd: $CaCl/NH_4OH$ 3rd: EtOH, KOH Ref. 48	Cool, 4°C, 24 hours	H_2O_2 oxidation	Turbidimetric, SO_4, Ref. 11, 13, 14

Continued

Table 5-7. (Continued) INORGANIC ANALYSIS METHODS FOR COAL GASIFICATION PROCESSES (GASEOUS)

Page 2

Gases	Sample Quantity Requirements	Container[1]	Collection System	Holding Time	Preparation	Analytical Method, Reference
Elemental Analysis:						
Impingers:	250 mls	P	HNO_3 & NaOH impingers	6 months	None	See Table 5-8 for liquid analyses
F		P	NaOH impingers Ref. 49	7 days	None	Specific ion electrode, Ref. 22
Cl		P	NaOH Impinger	7 days	None	Specific ion electrode, standard additions, Ref. 23
Metal Carbonyls (Fe, Ni)	Depends on concentration		I_2/HCl Impinger	6 months		Atomic Absorption, Ref. 24, AA Graphite Furnace
Solids	0.01 g		Particulates collected on filters		Acid digestion	See Table 5-9 for solids analyses

P - polyethylene
T - teflon
G - glass

Table 5-8. INORGANIC ANALYTICAL METHODS FOR COAL GASIFICATION PROCESSES (LIQUIDS)

Liquids	Sample Requirement	Container[1]	Preservation	Holding Time	Preparation	Analytical Method, Reference	Remarks
Acidity, total	100 mls	P, G	Cool, 4°C	24 hrs		Titrimetric, Ref. 11, 13, 14	
Alkalinity, total	100 mls	P, G	Cool, 4°C	24 hrs		Titrimetric, Ref. 11, 13, 14	
Biochemical oxygen demand (BOD)	1000 mls	P, G	Cool, 4°C	6 hrs		Bioassay, Ref. 11, 13	
Chemical oxygen demand (COD)	50 mls	P, G	H_2SO_4, pH <2	7 days	Dichromate reflux	Titrimetric, Ref. 11, 13, 14	
Chloride	100 mls	P, G		7 days	Interference removal, Ref. 13	Potentiometric titration using specific ion electrode, Ref. 13	Interference removal necessary due to organics & sulfur usually found in samples
Cyanide	500 mls	P, G	NaOH, pH >12 $PbNO_3$ to remove sulfide, Cool, 4°C	24 hrs	Distillation, Ref. 13	Spectrophotometric, Ref. 11, 13, 14	
Fluoride	500 mls	P	Cool, 4°C	7 days	Distillation, Ref. 13	Specific ion electrode, Ref. 11, 13, 14	
Hardness, total	100 mls	P, G	Cool, 4°C	7 days		Titrimetric, Ref. 11, 13, 14	
Nitrogen, ammonia	500 mls	P, G	H_2SO_4, pH <2, Cool, 4°C	24 hrs	Distillation, Ref. 11, 13, 14	Titrimetric, Ref. 11, 13, 14	
Nitrogen, nitrate	100 mls	P, G	H_2SO_4, pH <2, Cool, 4°C	24 hrs		Spectrophotometric, Ref. 13	
Oil & Grease	1000 mls	G, T	H_2SO_4, pH <2, Cool, 4°C	24 hrs		Soxhlet extraction, gravimetric, Ref. 11, 13	
Organic Carbon, total	100 mls	G, T (brown)	H_2SO_4, pH <2, Cool, 4°C	24 hrs		Carbonaceous analyzer, Ref. 11	
pH	25 mls	P, G	Determine on-site	6 hrs		pH meter, Ref. 11, 13, 14	

Table 5-8. (Continued) INORGANIC ANALYTICAL METHODS FOR COAL GASIFICATION PROCESSES (LIQUIDS)
Page 2

Liquids	Requirement	Container[1]	Preservation	Holding Time	Preparation	Analytical Method, Reference	Remarks
Phenol	500 mls	G, T	H_2SO_4, pH <4 1g $CuSO_4 \cdot 5H_2O$/1 Cool, 4°C	24 hrs	Distillation, Ref. 11, 13, 14	Spectrophotometric, Ref. 11, 13, 14	
Phosphate, total	100 mls	G (acid washed with 1:1 HNO_3)	Cool, 4°C	24 hrs	Acid digestion, Ref. 11, 13, 14	Spectrophotometric, Ref. 11, 13, 14	Ascorbic acid method
Residue: total, filterable, nonfilterable & volatile	400 mls	G, P	Cool, 4°C	7 days		Gravimetric, Ref. 11, 13, 14	
Specific conductance	100 mls	P, G	Cool, 4°C	24 hrs		Conductivity meter, Ref. 11, 13, 14	
Sulfate	50 mls	P, G	Cool, 4°C	7 days		Turbidimetric, Ref. 11, 13, 14	
Sulfide	100 mls	P, G	Zn acetate	24 hrs		Titrimetric, Ref. 11, 13	
Sulfite	100 mls	P, G	Cool, 4°C	24 hrs		Titrimetric, Ref. 11, 13, 14	
Temperature	1000 mls	P, G	Determine on-site	No holding		Ref. 13	
Elemental Analysis	1000 mls	P	HNO_3 to pH <2	6 months			
(Elemental Survey) (SSMS)	200 mls					Spark source mass spectrometry, Ref. 25	
Aluminum						Atomic absorption, Ref. 24, 25	
Antimony					Organic extraction, Ref. 38, 50	AA - graphite furnace, Ref. 11, 26, 27	
Arsenic						AsH_3 generation, Ag-DEDC pyridine, Ref. 11, 14	
Beryllium					Organic extraction, Ref. 39	Atomic absorption, graphite furnace. Ref. 11, 27	

Continued

Table 5-8. (Continued) INORGANIC ANALYTICAL METHODS FOR COAL GASIFICATION PROCESSES (LIQUIDS)

Page 3

Liquids	Requirement	Container[1]	Preservation	Holding Time	Preparation	Analytical Method, Reference	Remarks
Boron					Ion exchange Separation Ref. 40	Spectrophotometric, Ref. 28	
Cadmium					Ref. 36	AA - graphite furnace, Ref. 11, 27 Solvent Extraction - AA, Ref. 29	
Calcium						Atomic absorption, Ref. 11, 14, 24	
Chromium					Ref. 6	Atomic absorption, Ref. 11, 14 AA - graphite furnace, Ref. 27	0.1-5 mg/1
Copper					Ref. 6	Atomic absorption, Ref. 11, 14 AA - graphite furnace, Ref. 11, 27	0.1-5 mg/1
Iron						Atomic absorption, Ref. 11, 14, 24	
Lead					Solvent extraction, Ref. 29	Atomic absorption, Ref. 24 AA - graphite furnace, Ref. 11, 27	<0.3 ppm
Lithium						Atomic absorption, Ref. 14	1-5 mg/1
Magnesium						Atomic absorption, Ref. 11, 14, 24	
Manganese						Atomic absorption, Ref. 14 AA - graphite furnace, Ref. 27	0.04-5 mg/1 <0.1 mg/1
Mercury						Cold vapor, flameless atomic absorption, Ref. 11, 14, 30	
Molybdenum					Solvent extraction, Ref. 46	AA - graphite furnace, Ref. 27	
Nickel						Atomic absorption, Ref. 14 AA - graphite furnace, Ref. 27	0.2-10 mg/1 <0.2 mg/1
Potassium						Atomic absorption, Ref. 11, 24	
Selenium						Fluorometry, Ref. 31, 32, 33	
Silver					Ref. 6	AA - graphite furnace standard additions, Ref. 11, 27	
Silica						Atomic absorption, Ref. 24	
Sodium						Atomic absorption, Ref. 11, 24	
Thallium						Atomic absorption, Ref. 11, 24 AA - graphite furnace, Ref. 27	0.2-5 mg/1 <0.2 mg/1

Continued

Table 5-8. (Continued) INORGANIC ANALYTICAL METHODS FOR COAL GASIFICATION PROCESSES (LIQUIDS)
Page 4

Liquids	Requirement	Container[1]	Preservation	Holding Time	Preparation	Analytical Method, Reference	Remarks
Tin						Atomic absorption, Ref. 11, 24 AA - graphite furnace, Ref. 27	4-350 mg/1 <4 mg/1
Titanium						Spectrophotometric, Ref. 34	
Uranium						Fluorometry, Ref. 11, 35	
Vanadium						AA - graphite furnace standard additions, Ref. 27, 36	<1 mg/1
Zinc						Atomic absorption, Ref. 11, 24 AA - graphite furnace, Ref. 27	0.1-1 mg/1 <0.1 mg/1

[1] P = Polyethylene G = Glass T = Teflon

Table 5-9. INORGANIC ANALYTICAL METHODS FOR COAL GASIFICATION PROCESSES (SOLIDS)

Solids	Sample Requirements	Container	Preservation	Holding Time	Preparation	Analytical Method	Remarks
Inorganic Analysis:	1 kg	P			Ref. 37	Dry, crush, sieve, blend	
Morphology						Photometric photography, scanning electron microscope	
Ultimate Analysis: (C, H, O, N, S, Ash)	10 g					Ref. 37	
Proximate Analysis: (H_2O, ash, volatile matter, fixed carbon, Btu content)	10 g					Ref. 37	
Leachability Study	500 g	G,T	Cool, <4°C		Extract 24 hours with H_2O and/or dilute HCl	Elemental, anion, organic analysis	
Elemental Analysis:							
Elemental Survey (SSMS)	5 g					Spark source mass spectrometry, Ref. 25	
Elements: (Al, Ca, Fe, Mg, K, Si, Na)	50 g				$LiBO_2$ fusion, Ref. 51	Atomic absorption, Ref. 24	
P					Perchloric acid digestion	Colorimetry, Ref. 13	Ascorbic acid method
Ti					Perchloric acid digestion	Colorimetry, Ref. 34	
Sb					Perchloric acid digestion	Extraction, atomic absorption, Ref. 38	
As					Perchloric acid digestion	AsH_3 generation, AgDEDC-pyridine collection, Ref. 14	
Be					Perchloric acid digestion	Organic extraction, atomic absorption, Ref. 39	
B					Na_2CO_3 fusion, H_2SO_4 dissolution Ref. 41	Ion exchange separation , Ref. 40; colorimetry, Ref. 28	
Cd					Perchloric acid digestion	AA graphite furnace, Ref. 27; solvent extraction - AA, Ref. 29	

Continued

Table 5-9. (Continued) INORGANIC ANALYTICAL METHODS FOR COAL GASIFICATION PROCESSES (SOLIDS)

Page 2

Solids	Sample Requirements	Container	Preservation	Holding Time	Preparation	Analytical Method	Remarks
Cu					Perchloric acid digestion	AA, Ref. 14 AA - graphite furnace Ref. 27	
Cl					Na_2CO_3 fusion Ref. 42	Specific ion electrode, standard addition Ref. 41	
Cr					Perchloric acid digestion	AA, Ref. 14, AA, graphite furnace, Ref. 27	
F					Na_2CO_3 fusion Ref. 42	Specific ion electrode, standard addition Ref. 42	
Pb					Perchloric acid digestion	Solvent extraction - AA, Ref. 29, AA - graphite furnace, Ref. 27	
Li					Perchloric acid digestion	Atomic absorption, Ref. 14	
Hg					None	Gold amalgamation, cold vapor, flameless AA, Ref. 43, 44, 45	
Mn					Perchloric acid digestion	Atomic absorption, Ref. 14 AA - graphite furnace, Ref. 27	
Mo					Perchloric acid digestion	Solvent extraction, atomic absorption, Ref. 46	
Ni					Perchloric acid digestion	AA, Ref. 14; AA - graphite furnace, Ref. 27	
Se					Perchloric acid digestion	Organic extraction, fluorescence, Ref. 32, 47	
Ag					Perchloric acid digestion	AA - graphite furnace, standard additions. Ref. 27	

Continued

Table 5-9. INORGANIC ANALYTICAL METHODS FOR COAL GASIFICATION PROCESSES (SOLIDS)
Page 3 Continued

Solids	Sample Requirements	Container	Preservation	Holding Time	Preparation	Analytical Method	Remarks
Tl					Perchloric acid digestion	Atomic absorption, Ref. 24 AA - graphite furnace, Ref. 27	
Sn					Perchloric acid digestion	Atomic absorption, Ref. 24 AA - graphite furnace, Ref. 27	
U					Fusion, Ref. 35	Fluorescence, Ref. 35	
V					Perchloric acid digestion	AA - graphite furnace, standard additions, Ref. 27	
Zn					Perchloric acid digestion	Atomic absorption, Ref. 24 AA - graphite furnace, Ref. 27	

P - Polyethylene
G - Glass
T - Teflon

shown in Figure 5-4. This scheme is based upon the information given in Table 5-8.

Organic Analysis -

By comparing the inorganic species in Table 5-1 with the organic species listed in Tables 5-2 and 5-3, the complexity of quantitative organic analysis is readily apparent. The following discussion will provide the reader with descriptions of the tools available to the analyst and a general approach to guide the analyst in formulating a strategy for characterizing the organic species emitted from a specific coal gasification plant. A more detailed discussion of this subject is available in Assessment, Selection and Development of Procedures for Determining the Environmental Acceptability of Synthetic Fuel Plants Based on Coal, (Ref. 15). The general strategy outlined begins at the point where a sample is presented to the analyst. This strategy is presented in terms of:

- separation techniques,
- identification techniques,
- quantitative techniques, and
- integrated analytical scheme.

Samples from coal gasification processes that contain highly complex mixtures of organic species will require at least some degree of simplification by fractionation prior to identification and/or quantification. The examination of these fractions can then range in depth from the identification of functional groups which will indicate the presence or absence of classes of species to the quantification of individual species.

Separation Techniques - The separation techniques described here perform three primary functions. These functions are:

- removal of the species of interest from the sample matrix (solid, liquid, or sorbent),
- concentration of these species in a solvent

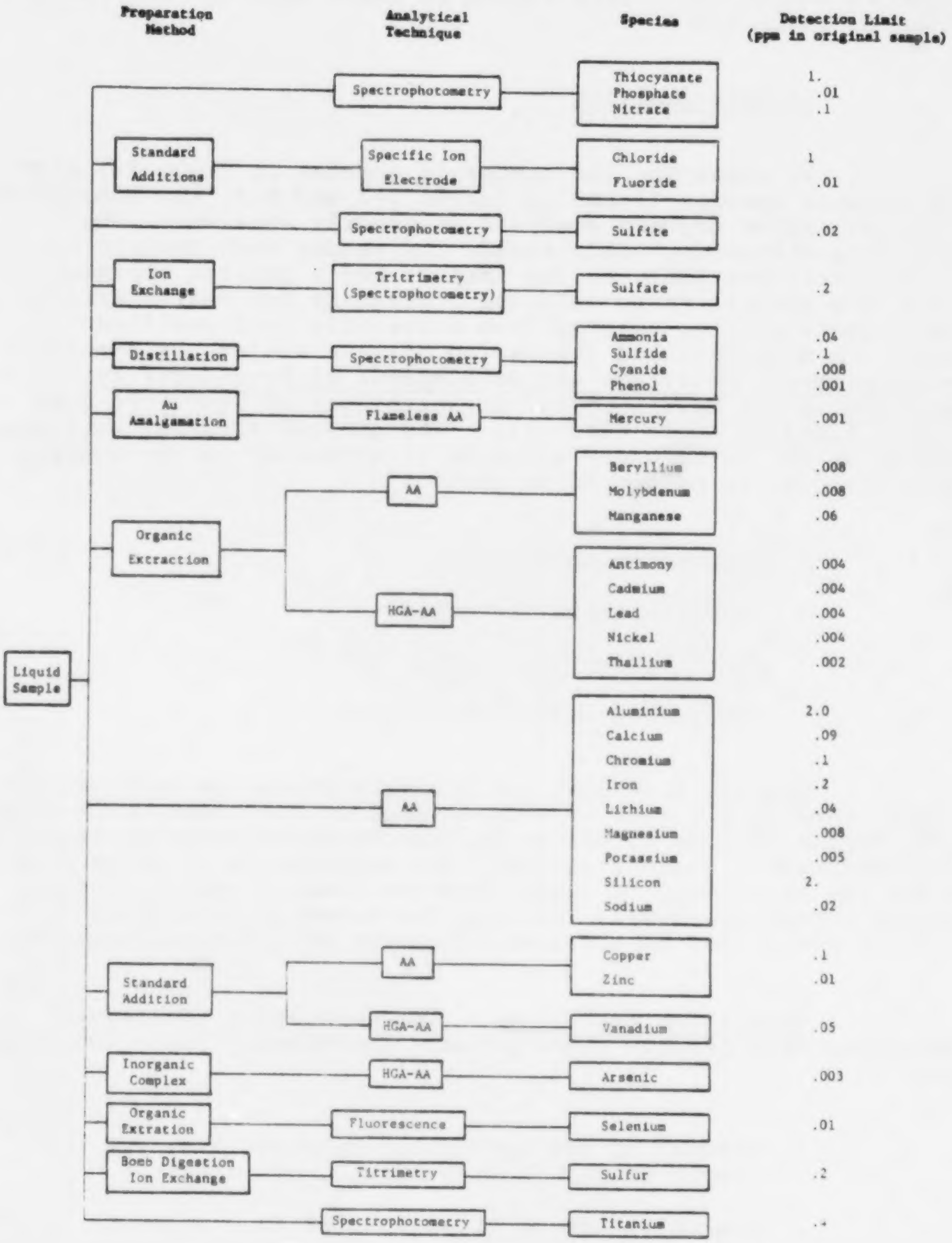

Preparation Method
Analytical Technique
Species
Detection Limit (ppm in original sample)
Liquid Sample
Spectrophotometry
Thiocyanate
Phosphate
Nitrate
1.
.01
.1
Standard Additions
Specific Ion Electrode
Chloride
Fluoride
1
.01
Spectrophotometry
Sulfite
.02
Ion Exchange
Tritrimetry (Spectrophotometry)
Sulfate
.2
Distillation
Spectrophotometry
Ammonia
Sulfide
Cyanide
Phenol
.04
.1
.008
.001
Au Amalgamation
Flameless AA
Mercury
.001
Organic Extraction
AA
Beryllium
Molybdenum
Manganese
.008
.008
.06
HGA-AA
Antimony
Cadmium
Lead
Nickel
Thallium
.004
.004
.004
.004
.002
AA
Aluminium
Calcium
Chromium
Iron
Lithium
Magnesium
Potassium
Silicon
Sodium
2.0
.09
.1
.2
.04
.008
.005
2.
.02
Standard Addition
AA
Copper
Zinc
.1
.01
HGA-AA
Vanadium
.05
Inorganic Complex
HGA-AA
Arsenic
.003
Organic Extration
Fluorescence
Selenium
.01
Bomb Digestion Ion Exchange
Titrimetry
Sulfur
.2
Spectrophotometry
Titanium
.4

Figure 5-4. EXAMPLE INORGANIC ANALYTICAL SCHEME FOR LIQUID SAMPLES

suitable for introduction into the remainder of the analytical scheme, and

- simplification of the sample by fractionation into groups containing fewer individual species.

The separation techniques which are considered applicable to samples from coal gasification processes include:

a) extractions from solid samples and sorbent materials,

b) liquid-liquid partitioning,

c) distillation,

d) inert gas stripping,

e) ion exchange,

f) gel permeation,

g) column chromatography,

h) gas chromatography, and

i) derivatization.

a) Extractions - Extractions from solid samples or sorbent materials should be performed in a Soxhlet extractor (Ref. 52 and 53) or similar device. The extraction solvent must be of high purity. Commercial solvents may require purification prior to use or characterization to quantify a reagent blank. The solvent should be volatile. Extractions should be conducted at as low a temperature as possible to avoid sample loss by volatilization or thermal decomposition. Poor extraction efficiencies should be rectified, if possible, by selecting alternate solvents rather than by increasing temperature.

Extraction of an aqueous sample can be performed batchwise, as in a separatory funnel, or in a continuous extractor. Saponification (Ref. 54) can provide a more thorough extraction by treating a dispersion of the solvent in the sample. However, emulsions must be avoided during extraction . In some situations, this may require the use of an alternate solvent. As with extrations from solids, sequential extractions with additional solvents may be required for better extraction efficiency.

b) Liquid-liquid partitioning - Liquid-liquid partitioning involves the transfer of selected species from one liquid phase to another. Species are separated on the basis of acid/base or polar/nonpolar character. Several aspects of liquid-liquid partitioning must be considered when designing a separation scheme using this technique.

- Distribution coefficients are a measure of the degree of partition achievable between two phases. Sequential partitioning with small volumes of the extractant which are then combined will result in a greater total efficiency than a single extraction with the same total solvent volume.
- Solvent volumes may become large enough for evaporative concentration to be required. Several techniques are available for concentration including a reduced pressure rotary evaporator, a Kaderna-Danish evaporator, freeze-drying and evaporation with an inert gas (Ref. 55, 56). The prime consideration here is to accomplish the solvent removal without loss of sample through volatilization or thermal decomposition.
- Solvent purity must be assured since solvent impurities can become concentrated in the sample. Continuous solvent purity checks should be an integral part of the analytical quality control program.
- Acid or base catalyzed reactions may result in the loss of specific sample components. Standards of reactive species should be carried through each step to identify reaction losses as part of the analytical quality control program.

c) Distillation - Steam distillation provides a means of separating species on the basis of volatility. Addition of an acid or base to the sample solution will add an additional dimension of separation by acid/base character. The problems discussed above for liquid-liquid partitioning apply in general to distillation. The potential for loss by reaction or thermal decomposition is even greater due to the elevated temperatures. This may be partially alleviated by vacuum distillation but the use of standards to check the procedure is still required.

d) Inert gas stripping - Inert gas stripping provides a feasible means of separating volatile species which would be lost in the evaporative concentration steps of other techniques. Non-polar species with boiling points below 100°C can be recovered. The species are stripped from the sample with a low flow of inert gas (<30 ml/min) and sorbed on Tenax or other sorbents. Recovery by thermal desorption allows direct introduction to a gas-chromatographic analyzer.

e) Ion-exchange - A separation scheme in which acids are removed on anion-exchange resins, bases on cation-exchange resins and neutral nitrogen compounds on $FeCl_3$/attapulgus clay has been applied extensively to petroleum analysis (Ref. 57,58). Potential problems with ion exchange procedures include reproducibility, resin swelling, acid resin catalysis of reactions, extremely long separation times, and losses of trace components.

f) Gel-permeation chromatography (GPC) - Gel permeation chromatography is an exclusion technique in which retention is based on molecular size. Molecules too large to penetrate the support media pores are eluted with the solvent while smaller molecules are selectively retained. GPC support media are available in a variety of pore sizes ranging from <50°A to >3000°A. The mobile phase (solvent) is chosen on the basis of low viscosity, dissolution properties and compatibility with the support media.

g) Column chromatography - The types of liquid chromatography generally applicable for separating coal conversion process samples are: 1) nonlinear elution chromatography, 2) linear-elution chromatography, and 3) reversed-phase chromatography. Nonlinear-elution chromatography uses an active support media which tightly binds selected species until they are eluted with a different solvent. The sequential use of several solvents or mixtures will result in an equal number of discrete fractions. Linear-elution chromatography uses a less active support media which binds species in varying degrees resulting in continually eluting bands in a single solvent or a series of solvent mixtures of gradually increasing polarity. Reversed-phase chromatography is performed on a non-polar support with polar solvents.

h) Gas chromatography - Gas chromatography is a technique widely applied in qualitative and quantitative analysis but its value as a preparative separation procedure is often ignored. Preparative scale gas chromatography (PSGC) is in essence a scale-up of systems more generally used in qualitative and quantitative analysis. The inlet to the column must be designed to ensure flash evaporation of the larger sample quantities involved or severe tailing and incomplete separation will result. Fractions eluting from the column may be collected by condensation or sorption on a suitable support medium.

i) Derivatization - Derivatization is a technique by which a component of interest is, through selective reaction, converted to a compound which is compatible with a separation, identification or quantification technique. The most generally applied derivatization technique is methylation. Many methylation agents are available and a general discussion of their applications has been provided by Webb, et. al. (Ref. 56).

Identification Techniques - Many of the techniques utilized in organic analysis provide both identification and quantification. This section will deal with those techniques which are primarily applied only to identification and for which quantification is difficult or only feasible in specialized situations. Some of these techniques can provide semi-quantitative data without extensive calibration or development; however, the accuracy and precision expected of quantitative techniques is impossible or extremely difficult to attain. These identification techniques include:

a) high-performance liquid chromatography,

b) thin-layer or paper chromatography,

c) functional group analysis,

d) mass spectrometry,

e) nuclear-magnetic resonance spectrometry, and

f) infrared spectrometry.

An analytical separation (as opposed to gross or class preparative separations) is an integral part of some of these techniques.

a) High-performance liquid chromatography (HPLC) - The major advantage of HPLC is its ability to separate very polar compounds without derivatization, highly reactive compounds, and compounds which have very low vapor pressure or are thermally labile. HPLC is a relatively new technique still undergoing a great deal of development but of great utility in the analysis of very polar water-soluble species. Column packing alternatives include porous silica spheres, liquid phase coated support, bonded phases and ion exchange materials. Elution solvents are selected to be compatible with both the sample and the column packing material, and may range from aqueous solutions to non-polar organic solvents. The use of sequential elution with varying strength solvents or solvent mixtures is particularly useful for complex mixtures.

The detectors for HPLC are typically either a differential refractometer or a fixed wavelength ultraviolet (U.V.) cell. Differential refractometers measure differences in refractive index between pure solvent and solvent containing solute. Although responsive to all compounds, they are inherently insensitive. U.V. cells are the most widely used HPLC detector and, depending on the U.V. absorption characteristics of the compound, is much more sensitive than the refractometer. Recent developments have provided U.V. cell detectors with variable wavelength capabilities.

Identification of compounds is achieved in HPLC through comparison of retention time with standards and, to a limited extent, examination of U.V. absorption and refractive index.

b) Thin-layer chromatography (TLC) - This chromatographic technique has limited utility analysis, but its analytical separation capability combined with specific visualization reagents, fluorescene, and fluorescence quenching, make it useful for general detection. Standards which must be run with each unknown TLC may also serve as a useful analytical preparative technique since the spots may be removed and subjected to analysis by other techniques.

c) Functional group analysis - Functional group detection by spot test is not useful for the identification of individual compounds but provides an inexpensive, "quick and dirty" check for a given functional group. Spot tests have been developed for almost every known functional group or combination of functional groups (Ref. 59). Spot tests can be used in the field to provide a quick indication of the presence of a class of compounds or in a complex analytical scheme to check the efficiency of separations or derivatizations.

d) Mass spectrometry - There are two general categories of mass spectrometry which are decidedly different in their applications:

High-resolution (HRMS), and

Low-resolution (LRMS).

The primary value of HRMS is the determination of possible presence or certain absence of preselected compounds. The accurate mass determination of HRMS will often provide definitive identification if mixtures are not overly complex. HRMS is not capable of distinguishing between isomers and often cannot offer data for differentiating between compounds of isoatomic structures.

LRMS cannot give the precision of mass that HRMS supplies since it only measures integral mass numbers. It does, however, offer several advantages including fast scans over a wide mass range and chemical ionization. It can be combined with gas chromotagrphy (GC-MS). The fast scan capability of LRMS provides data over a large range of mass with a limited sample quantity. Chemical ionization can help indicate the molecular weight of a compound. GC-MS combines the separation capabilities of gas chromatography with the identification capability of mass spectrometry to provide the most powerful analytical tool available today. More detailed discussions of GC-MS will be provided in the section on quantitative analysis.

e) Nuclear magnetic resonance spectrometry (NMR) - NMR has very limited use in an identification scheme for trace organic compounds contained in complex mixtures. For pure or relatively pure samples in sufficient quantity NMR may provide adequate information for complete identification. Some of the sensitivity limitations can be overcome by Fourier Transform NMR (Ref. 60), but the specificity limitations remain.

f) Infrared spectrometry (IR) - IR suffers from the same sensitivity and specificity limitations as NMR. The greatest application of IR is its power to indicate the presence of various functional groups through correlation with reference spectra. The sensitivity of IR can be enhanced through the use of attenuated total reflection (ATR). Advantages of ATR include ease of sample preparation, extreme sensitivity, and non-destructive analysis. Another recently developed IR technique is Fourier Transform Infrared (FTIR) which provides enhanced sensitivity over conventional IR. FTIR can be used to scan peaks from a gas chromatograph as they emerge.

Quantification Techniques - Three organic quantitative analytical techniques are discussed here:

a) Gas Chromatography (GC),

b) Gas Chromatography - Mass Spectrometry (GC-MS), and

c) Colorimetry.

Gas chromatography is the most widely used technique for both identification and quantification of organic compounds available today. Gas Chromatography-Mass Spectrometry is treated separately because of the unique power of this combination. Colorimetric techniques were widely used in the past but due to their limitations are currently secondary to GC and GC-MS.

a) Gas Chromatography (GC) - A wide variety of separation capabilities can be accomplished using various column configurations and a number of detection systems. Identification is based on the comparison of retention times with those of standards and the use of selective detectors. The instrument must be extensively calibrated for retention time measurements. Quantitation is accomplished by comparison of detector response for an unknown with a calibration curve prepared from standard solutions of the same compound. Detector response will vary with instrument conditions (flow rates, oven temperatures, and maintenance of the instrument), compound identity and column type. The use of literature "response factors" that relate the response of a detector for various compounds to a common basis is not adequate for quantification unless the response factors were generated on the instrument in use at the same operating conditions.

Several detectors are available which lend a great deal of flexibility and specificity to GC analysis.

- Flame Ionization Detectors (FID) - The FID is a useful detector for quantification because of its wide linear range, sensitivity, good response to high concentrations, insensitivity to temperature and pressure changes, and response to all organic compounds of interest except formic acid and carbon disulfide. FID response is in general proportional to sample weight rather than molar concentration.

- Electron Capture Detector (ECD) - The ECD is much more responsive to electronegative compounds than to other types. It is suitable for polynuclear aromatics, nitrated, chlorinated and perfluorinated compounds. The ECD is highly sensitive to these groups of compounds but is limited by a small linear dynamic range. Sensitivity and response vary widely from compound to compound requiring calibration for each compound over the full range of expected concentration.

- Thermal Conductivity Detectors (TC) - TC detectors are relatively insensitive by comparison to FID or ECD and are, therefore, most useful for higher concentration characterization for inorganic gases or volatile organics.

- Conductivity Detectors - The electrolytic conductivity detector is commonly called the Coulson or Hall detector (a much improved version). This detector combines catalytic combustion in a controlled atmosphere with dissolution of the combustion products in an electrolyte. The resulting variations of electrolytic conductivity are measured. The detector is sensitive to sulfur-containing and halogenated compounds when the combustor operates in the oxidative mode. The detector is sensitive to nitrogen-containing compounds when the combustor operates in the reductive mode.

- Flame-Photometric Detector (FPD) - The FPD can be made specific to sulfur or phosphorus-containing compounds by the appropriate choice of interference filters which pass either the sulfur or phosphorus emission bands. The detector is highly sensitive (0.001 μg, or less) but is totally nonlinear.

b) Gas Chromatography-Mass Spectrometry (GC-MS) - Gas chromatography-mass spectrometry (GC-MS) combines separation, identification, and quantification. Both GC retention time and mass spectra are used for identification. Quantification can be achieved by three techniques: auxiliary GC detector, total ion current monitoring, and selected ion monitoring. The use of an auxiliary GC detector is identical to quantification by GC alone, while total ion monitoring is similar with the mass spectrometer serving as the detector. Selected ion monitoring (SIM) also uses the mass spectrometer as a GC detector but greatly increases sensitivity and specificity. Either the electron impact or chemical ionization mode may be used for quantification.

A GC-MS system normally includes four major components: the gas chromatograph, the mass spectrometer, an interface between the two and a computerized data system. Gas chromatography has been previously discussed. Both magnetic sector and quadrapole mass spectrometers have been used. Quadrapole instruments have rapid scan time and can perform multiple SIM scans simultaneously. The interface between the GC and MS consists of a molecular separator of which there are three categories: 1) enrichment by effusion, 2) enrichment by preferential effusion through a semipermeable membrane, and 3) fractionation in an expanding jet stream. All of these are designed to enrich the concentration of the solute in the carrier gas. The rapidity with which a GC-MS system generates data makes the availability of a dedicated computerized data system a virtual necessity.

c) Colorimetry (Ultraviolet-Visible Spectrometry) - The greatest utility of UV-visible techniques is in quantitation. A limited amount of qualitative information may be obtained from evaluation of spectral scans, but the information is limited in sensitivity and specificity. Quantification depends on the presence of a unique absorption band either for the compound of interest or some derivative. It is based on the Beer-Lambert Law and concentrations are determined from a calibration curve generated from standard solutions. The technique of standard additions may be useful for eliminating matrix interferences.

Integrated Scheme for Organic Analysis - Now that the techniques available to the analyst have been briefly described, it is necessary to consider how these can be applied in some logical manner to the characterization of a sample from a coal conversion process. Figure 5-5 provides an example of such an integrated scheme which is designed to apply to solid, liquid, or gaseous samples. This scheme relies heavily on the use of gas chromatography-mass spectrometry for the final identification and quantification of organic compounds and includes some inorganic components to indicate the beginnings of the total integration of the analytical function which is ultimately required.

The operations in the upper part of Figure 5-5 provide examples of gaseous species, both organic and inorganic, which are determined on-site or with minimal preparation prior to off-site analysis. Immediate analysis of the reactive gases is required because of their instability. These include carbonyl sulfide, carbon disulfide, hydrogen sulfide, methyl mercaptan, methyl amine, hydrogen cyanide and other low molecular weight sulfur and nitrogen species. The nonreactive gases include low molecular weight hydrocarbons and "fixed" inorganic gases such as oxygen, nitrogen, carbon dioxide. Acid gases trapped in a KOH impinger include inorganics and organics such as carboxylic acids, phenols, sulfonic acids and aryl thiols. Basic gases, such as low molecular weight amines and ammonia, will be collected in an acidic impinger. Aldehydes are easily oxidized and thus should be collected as the more stable aldoximes, hydrolyzed with HCL, and then analyzed as aldehydes by GC.

General reference sources which should prove useful in the analysis of organic compounds include:

- Identification and Analysis of Organic Pollutants in Water, L.H. Keith, 1976 (Ref. 61);
- Current Practices in GC-MS Analysis of Organics in Water, Webb, Garrison, Keith and McGuire (Ref. 56);
- Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants, Revised, April 1977, EPA (Ref.6);
- Techniques of Combined Gas Chromatography/Mass Spectrometry, McFadden, 1973 (Ref. 62); and

- Assessment, Selection, and Development of Procedures for Determining the Environmental Acceptability of Synthetic Fuel Plants Based On Coal, (Ref. 15).

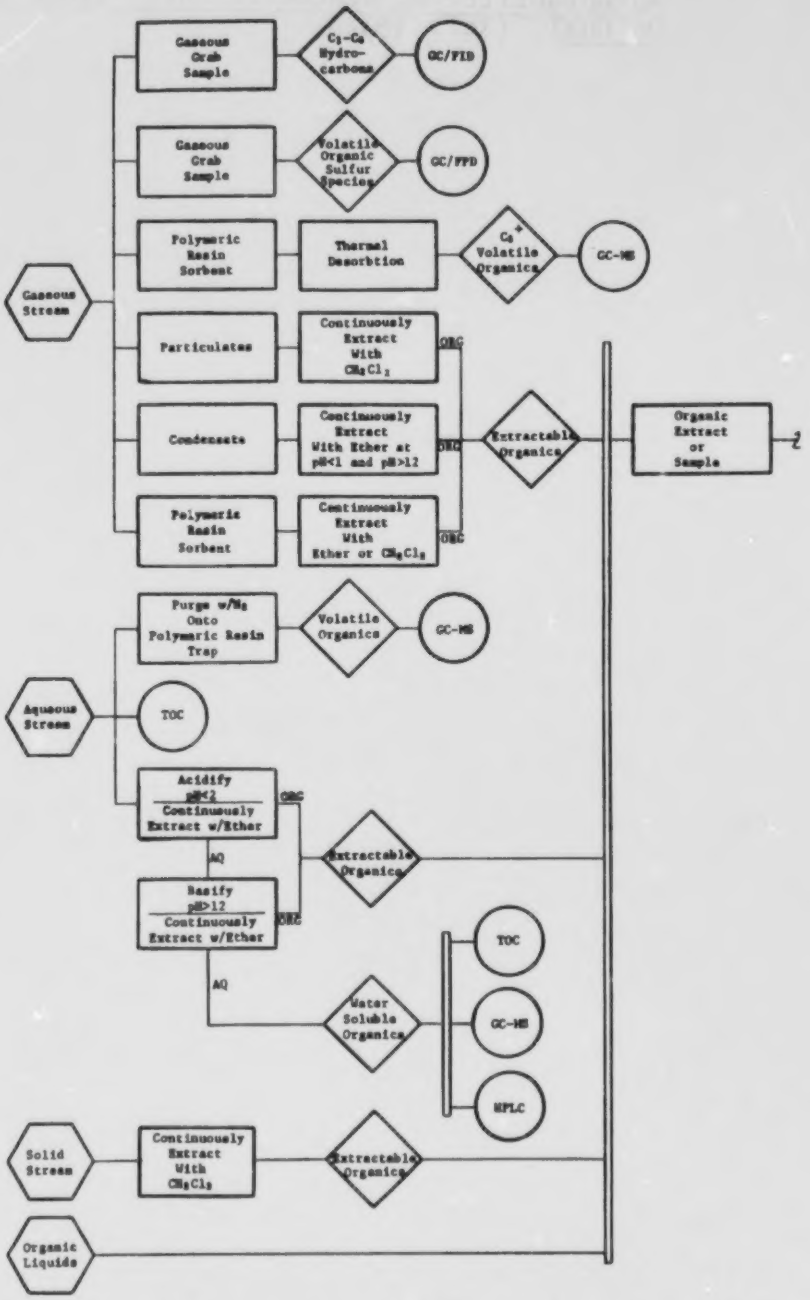

Gaseous Grab Sample
C_1-C_6 Hydrocarbons
GC/FID
Gaseous Grab Sample
Volatile Organic Sulfur Species
GC/FPD
Polymeric Resin Sorbent
Thermal Desorbtion
C_6^+ Volatile Organics
GC-MS
Gaseous Stream
Particulates
Continuously Extract With CH_2Cl_2
ORG
Condensate
Continuously Extract With Ether at pH<1 and pH>12
ORG
Extractable Organics
Organic Extract or Sample
2
Polymeric Resin Sorbent
Continuously Extract With Ether or CH_2Cl_2
ORG
Purge w/N_2 Onto Polymeric Resin Trap
Volatile Organics
GC-MS
Aqueous Stream
TOC
Acidify pH<2 Continuously Extract w/Ether
ORG
AQ
Extractable Organics
Basify pH>12 Continuously Extract w/Ether
ORG
AQ
TOC
Water Soluble Organics
GC-MS
HPLC
Solid Stream
Continuously Extract With CH_2Cl_2
Extractable Organics
Organic Liquids

Figure 5-5a. INTEGRATED SCHEME FOR SEPARATION AND ANALYSIS OF ORGANIC CONSTITUENTS FROM COAL GASIFICATION PROCESSES

LEGEND:

LC - Liquid chromatography
ORG - Organic solvent phase
AQ - Aqueous phase
ALC - Alcoholic (MeOH or EtOH)
GRAV - Gravimetric analysis
GC-MS - Combined gas chromatography - mass spectrometry analysis
TCO - Total chromatographable organics analysis by GC-FID (C_7-C_{17})
TOC - Total organic carbon analysis
HPLC - High pressure liquid chromatography
GC/FID - Gas chromatography using flame ionization detector
GC/FPD - Gas chromatography using flame photometric detector

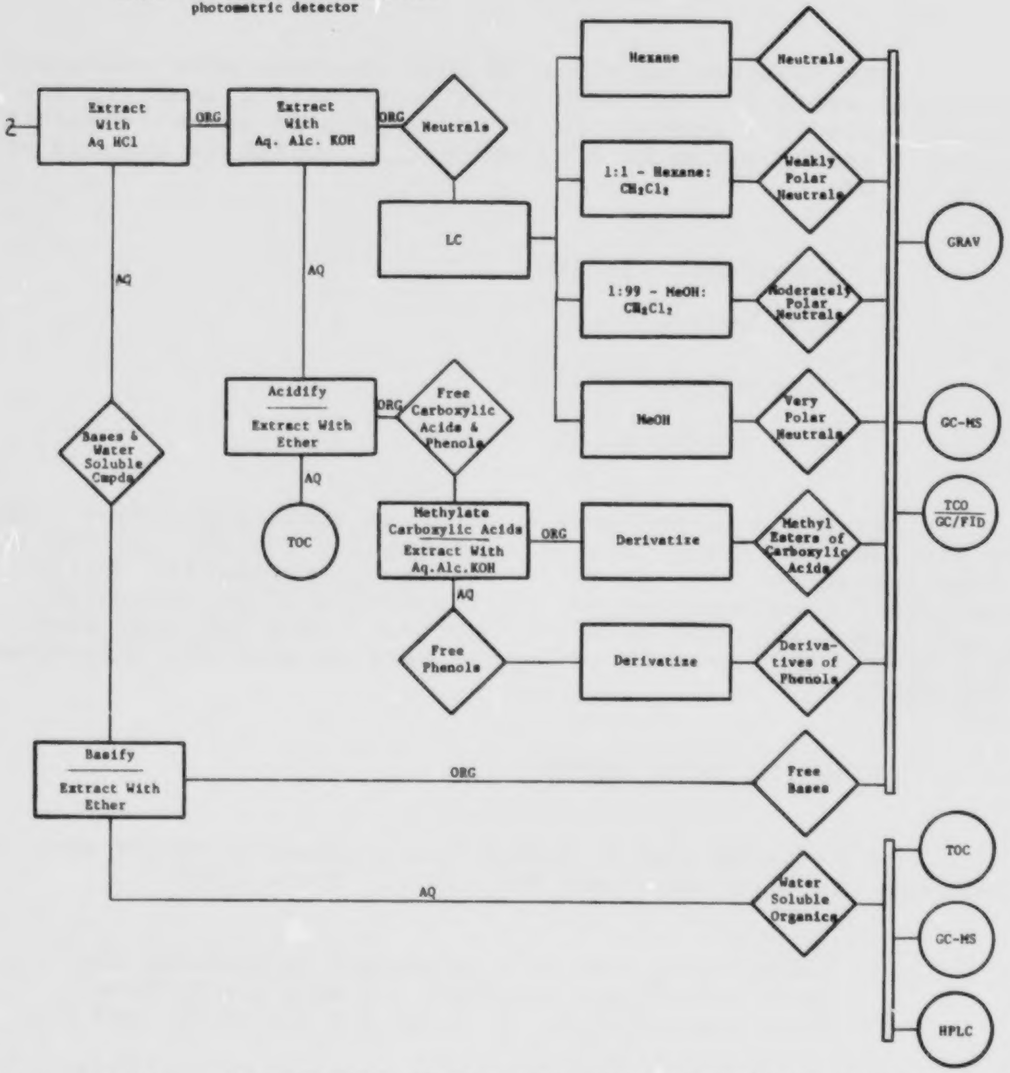

2
Extract With Aq HCl
ORG
Extract With Aq. Alc. KOH
ORG
Neutrals
LC
Hexane
Neutrals
1:1 - Hexane: CH_2Cl_2
Weakly Polar Neutrals
1:99 - MeOH: CH_2Cl_2
Moderately Polar Neutrals
MeOH
Very Polar Neutrals
GRAV
GC-MS
TCO
GC/FID
AQ
AQ
Acidify
Extract With Ether
ORG
Free Carboxylic Acids & Phenols
Bases & Water Soluble Cmpds
AQ
TOC
Methylate Carboxylic Acids
Extract With Aq.Alc.KOH
ORG
Derivatize
Methyl Esters of Carboxylic Acids
AQ
Free Phenols
Derivatize
Derivatives of Phenols
Basify
Extract With Ether
ORG
Free Bases
AQ
Water Soluble Organics
TOC
GC-MS
HPLC

Figure 5-5b. INTEGRATED SCHEME FOR SEPARATION AND ANALYSIS OF ORGANIC CONSTITUENTS FROM COAL GASIFICATION PROCESSES

SECTION 6.0

DATA MANAGEMENT

The previous sections of this document have addressed the general areas of test objectives, engineering analysis and sampling/analysis. Another important aspect of an environmental assessment test program is data management, which is assumed here to consist of:

- experiment planning,
- data validation,
- data evaluation, and
- data handling.

From a data management point of view, experiment planning involves the establishment of a quality control program and, in some instances, the use of statistical experimental design procedures. Consideration of how the data will be validated, evaluated, and reported is also important since this may identify potential problems in using the data to meet the objectives of the test.

6.1 PLANNING EXPERIMENTS

A properly executed experiment planning effort should accomplish two very important functions. These are:

- identifying the data necessary to satisfy the test objectives (portions of this point have been discussed in Sections 2.0 and 3.0), and
- providing a method for ensuring that the data obtained are accurate.

To accomplish these objectives, sound experimental and quality control programs must be developed. The details of an experimental program need to be established early in the test plan since its design affects and is affected by the sampling and analysis methods to be used. A quality control program is needed to minimize the propagation of determinative errors (bias) through the sampling/analysis/evaluation chains of the test program.

6.1.1 Statistical Experimental Design

From a statistical point of view, experimental design is concerned with the planning of an experiment or set of experiments so that the resulting data can be used to answer the questions of the experimenter through the use of statistical analysis. It also provides a set of rules for collecting samples. Although data from normal operating logs can sometimes be used for regression analysis or analysis of variance, an experimental design provides assurance that all data needed to satisfy the experimental goals will be collected. The following discussion serves basically to introduce the subject. The classic work by Cochran and Cox (Ref. 53) is strongly recommended for a detailed approach. Perry's Chemical Engineer's Handbook (Ref. 64) also provides a good introduction with specific applications to process experimentation.

Three types of experimental designs which have applicability to quantitative waste stream and control equipment testing are:

- full factorial,
- fractional factorial, and
- Box-Wilson.

In order to illustrate the significant characteristics of these techniques, the following examples have been prepared. Consider an experiment where the effects of volume flow rate (V) and temperature (T) on SO_2 emissions from a control process are to be assessed. Assume 3 levels of flow rate and 3 levels of temperature will be studied in the experiment A full factorial experimental design would appear as in Figure 6-1, and would consist of 9 different tests.

	V_1	V_2	V_3
T_1	V_1T_1	V_2T_1	V_3T_1
T_2	V_1T_2	V_2T_2	V_3T_2
T_3	V_1T_3	V_2T_3	V_3T_3

Figure 6-1. A FULL FACTORIAL DESIGN INVOLVING TWO INDEPENDENT VARIABLES AT THREE LEVELS

The number of tests required for a full factorial design rapidly becomes excessive as the number of variables and/or the number of test levels increase. Fractional factorial and Box-Wilson designs are procedures for reducing the number of tests required from that of a full factorial design. The fractional design uses an integer fraction (a multiple of the number of test levels) of the number of tests required by the full factorial design. For example, a 1/3 fractional design for an experiment involving 4 variables at 3 test levels ($3^4 = 81$ possible tests) would consist of 27 tests. The combinations of levels to be tested are chosen randomly. Two National Bureau of Standards (NBS) documents (Ref. 65 and 66) provide tabulations of factorial designs for variables tested at three levels and two levels, respectively.

Box-Wilson designs approach the problem from a process modeling viewpoint, but the end result is the same, *i.e.*, the number of required tests is reduced in a random fashion. A general set of experiments has been designed to derive the mathematical model of the process. The experimental design includes three types of independent variable combinations: axial, factorial and center. Axial points consist of each variable at its extreme points (maximum and minimum), while all other variables are at their mid-points. The factorial points include all combinations of intermediate levels (*i.e.*, extreme points are omitted). The center point consists of all variables at their mid-points, and is usually repeated several times for purposes of estimating error.

6.1.2 Quality Control Program

A quality control program needs to be developed during the planning stage of a sampling and analysis program in order to ensure that the data obtained are accurate. Developing a sound quality control program involves:

- estimating the expected variability of the data,
- estimating the error propagation through the sampling/analysis chains of the program, and
- selecting methods for maintaining sampling and analytical accuracy.

Estimates of data variability and error propagation involve interplay with the engineering analysis and with the selection of sampling and analysis techniques. Because data variability and error propagation are also important concerns in data validation, these areas will be discussed in Section 6.2.

The methods which can be used to maintain a quality control program are relatively simple and generally should be performed in the field to ensure rapid feedback of information when a loss of control is indicated. The two most common types of analysis are the use of correlation tests and the maintenance of control charts.

One of the most important techniques for maintaining accuracy in a sampling/analysis chain is the regular use of alternative pairs of results determined by two different methods. Correlation analysis of data pairs will indicate the degree to which the results are similar. (They do not have to be identical, but they must be linearly related.) To ascertain whether apparent differences in the results are real, several common statistical methods may be used, such as confidence intervals, t-tests, or F-tests. (Refer to any statistical methods book, such as Ref. 67 or 68.)

For daily maintenance of quality control, an excellent technique is the use of a quality control chart, such as the Shewhart Control Chart (Figure 6-2). These charts can be used to display such quality control data as: replicate sample results,

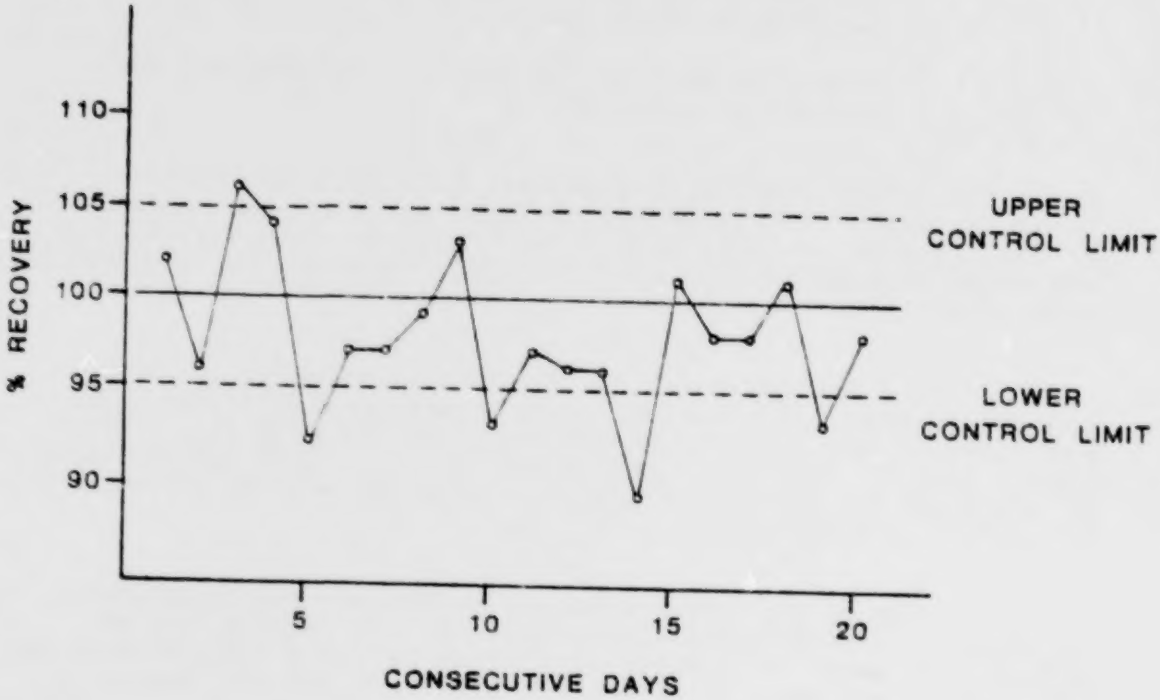


Figure 6-2. EXAMPLE OF A QUALITY CONTROL CHART FOR SPIKED SAMPLES (REF. 5).

isokinetic sampling rates, EPA sampling train calibration factors, and "spiked" sample recovery results. For most applications, the control limits are set at three standard deviations (3σ) for replicate results. The initial estimates of σ can be based on previous results or on laboratory results. Later, a running estimate of the pooled standard deviation should be maintained for setting the control limits. If any variations that are outside of the control limits occur, the source of the problem should be identified and corrective measures should be taken.

If a detailed evaluation of the sources of error in the sampling and analysis chain is needed, analysis of variance can be used. However, this procedure requires replication at every stage of sampling and analysis at which variations can occur. In most field testing, this is impractical.

6.2 DATA VALIDATION

The importance of data validation to a successful sampling and analysis program cannot be overemphasized. In order to draw meaningful conclusions and recommendations, test results must be validated. After the analytical results have been transformed into stream concentrations (*i.e.*, data reduction), useful data validation techniques include material balance and statistical calculations. Test results should also be compared with expected results, *i.e.*, estimates based on engineering calculations or the results of previous tests of a similar nature.

6.2.1 Material Balance Calculations

As stated previously, material balance tests around a process are usually performed on an element (*e.g.*, sulfur). If the results of the element balance indicate that the amount of the element entering a process does not equal (within experimental error) the amount exiting the process, the methods used to measure stream flow rates, collect the samples and analyze the element need to be checked and corrective procedures initiated.

It should be emphasized that closure of a material balance does not mean that there are no errors in the sampling, analytical or stream flow rate determination techniques. For example, errors in flow rate measurement may offset errors in sample collection and/or analysis. To minimize this problem, instrument maintenance calibrations should be performed frequently during the test.

6.2.2 Statistical Data Validation

Methods for estimating data variability should be considered in all test plans. Several statistical quantities useful in measuring data variability are:

- mean value - the arithmetic average of a set of data,
- sample standard deviation - a measure of the distribution of a set of data about the calculated mean value,
- confidence interval - a range about the calculated mean wherein a certain percentage of the measured data should lie if they are normally distributed (*e.g.*, the probability for a measurement to fall within one sample standard deviation of the mean is about 68%; two sample standard deviations is about 95%), and
- error propagation - a measure of the cumulative error in a value due to error in the methods used to obtain the value (for the case of test data, the error is introduced by the sampling and analytical techniques).

It is not the intent of this document to present a detailed discussion of statistics. Instead, reference is made to the excellent works by Snedecor and Cochran (Ref. 67) or Bowker and Lieberman (Ref. 68).

6.3 DATA EVALUATION

The types of data evaluation techniques required are dependent upon the objectives of the test. In the following text, data evaluation techniques for typical waste stream, control equipment, and process stream characterization tests are discussed. Specific examples are also given in order to help explain the evaluation procedures.

6.3.1 Waste Stream Characterization Test

As discussed in Section 2.0, waste stream characterization tests are grouped into three test types: screening tests (Level 1), quantitative tests (Level 2), and continuous monitoring (Level 3). Data evaluation procedures for each of these tests are discussed below.

Level 1 Screening Test -

The primary objective of a Level 1 waste stream characterization test is to identify the potentially hazardous waste streams that need to be further characterized. Identification of these streams is achieved by performing both chemical analysis and bioassay tests. A detailed discussion of the procedures for reducing and evaluating the raw Level 1 chemical data is presented in two draft reports: Approach to Level 2 Analysis Based on Level 1 Results, MEG Categories and Compounds and Decision Criteria (Ref. 69), and Suggested Report Format for Level 1 Organic Analysis Data (Ref. 70). A brief discussion of the procedures used to reduce Level 1 chemical and biological data and to identify potentially hazardous waste streams is discussed in the following text.

Level 1 Chemical Data - In order to reduce the raw chemical data obtained from a Level 1 test, organic data from liquid chromatography (LC), gas chromatography (GC), infrared spectroscopy (IR), low resolution mass spectrometry (LRMS), and spark source mass spectrometry (SSMS) need to be converted to concentrations (mass loadings) of compounds or compound classes (*e.g.*, phenols) in the waste stream sample. These concentration values may be reported in $\mu g/m^3$ for gases, $\mu g/g$ for solids and $\mu g/\ell$ for liquids. These concentrations are then compared with appropriate decision criteria values in making a judgment on whether further characterization is necessary. It is currently recommended that minimum acute toxicity effluent (MATE) values be used as these decision criteria. These MATE values are given in Multimedia Environmental Goals for Environmental Assessment (Ref. 71).

MATE values are specific for individual chemical species while the results obtained from Level 1 tests give concentrations primarily for compound classes with only a limited number of specific compound concentrations. Therefore, for each category that is found in the sample, the worst chemical that could be present is used as a comparison value. In the cases where LRMS is used, specific compounds will be identified and their concentrations should be compared to their respective MATE values.

The following is a general procedure for analyzing the results of a Level 1 waste stream characterization test.

1. List the categories of compounds found in the sample by MEG category number and estimated concentration.
2. For each MEG category, identify the compound with the lowest MATE value (Ref. 69).
3. If the estimated concentration in the stream is lower than this MATE value, go to the next category.
4. Review the data to see if there is any evidence that the compound with the lowest MATE value cannot be present in the sample. This may be indicated from LRMS data on molecular weight ranges of the compounds present in the samples.
5. If the compound with the lowest MATE value can be ruled out, identify the compound with the next lowest MATE value and reiterate steps 3, 4, and 5 until MATE values have been selected for each category.
6. List the compounds and their MATE values selected for comparison between the estimated concentrations calculated from the Level 1 test.
7. If the estimated concentration values are greater than the MATE values, the stream or stream fraction may need further characterization.

An example of a Level 1 organic analysis results reporting format is given in Table 6-1. This table shows the MEG category and number, estimated concentration from the organic analysis of the sample, the MATE value of the most hazardous compound in

Table 6-1. LEVEL 1 ORGANIC ANALYSIS RESULTS COMPARED TO MATE VALUES

Category Found	MEG Number	Concentration Found mg/m^3	Lowest MATE in Category (compound) *	Ratio Found/MATE
Fused Aromatics >216 MW	21, 22	5	2.0×10^{-5} mg/m^3 (benzo[a]pyrene)	2.5×10^5
Fused Aromatics <216 MW	21, 22	5	30 mg/m^3 (methylphenanthrenes)	0.2
Heterocyclic N Compounds	23	1	16 mg/m^3 (quinoline)	0.06
Carboxylic Acids	8A, B	1	6 mg/m^3 (phthalic acid)	0.2
Sulfur Compounds	53	0.6	1 mg/m^3 (sulfuric acid)	0.6
Heterocyclic S Compounds	25	0.5	1 mg/m^3 (benzonapthothiophene)	0.5
Heterocyclic O Compounds	24	0.3	590 mg/m^3 (tetrahydrofuran)	0.0005
Phenols	18	0.1	2 mg/m^3 (1,4-dihydroxybenzene)	0.05
Esters	80	0.08	5 mg/m^3 (phthalates)	0.02
Aromatics Benzenes	15	0.06	1 mg/m^3 (biphenyl)	0.06
Aliphatic HC's	1	0.06	200 mg/m^3 (cyclopentadienes)	0.0003

* eliminating compounds that cannot possibly be present.

Table 6-2. BIOASSAY TEST RESULTS FOR A COAL GASIFICATION FACILITY

	Coal Feed	Barrel Valve Vent Gas*	Barrel Valve Vent Gas XAD-2 Extract*	Gasifier Ash*	Cyclone Dust*	Tar	Separator Vent Gas XAD-2 Extract*	Separator Liquor
HEALTH TESTS								
1. AMES	SP	-	P	N	N	P	SP	N
2. Cytotoxicity[a]								
WI-38, EC-50 (cell count, μg solid, m^3 gas/ml culture)	>60(s)	-	4×10^{-6}(g)	-	-	-	7×10^{-6}(g)	-
RAM, EC-50 (cell count, μg solid and liquid, m^3 gas/ml culture)	>1000(s)	-	>2×10^{-5}(g)	>300(s)	>1000(s)	>1000(s)	>1×10^{-5}(g)	>600(l)
3. Rodent Acute Toxicity	M	-	-	L	M	H	-	L
LD-50 (g sample/kg rat)	>10	-	-	>10	>10	>10	-	>10
ECOLOGICAL TESTS								
Fresh Water[b]								
Algal, EC-50 (15 days	-	-	-	-	-	-	-	1.0 to 0.1%
Daphnia, LC-50 (48 hours)	-	-	-	-	-	-	-	0.11%
Fathead minnow, LC-50 (96 hours)	-	-	-	-	-	-	-	0.02%
Salt Water[b]								
Algal, EC-50 (12 days) Filtered/ unfiltered	-	-	-	-	-	-	-	0.53/0.41%
Shrimp, LC-50 (96 hours)	-	-	-	-	-	-	-	0.25%
Sheepshead minnows, LC-50 (96 hours)	-	-	-	-	-	-	-	0.16%
Terrestial								
Soil microcosm[c]	3	-	-	4	1	2	-	5
Plant stress ethylene	-	N	-	-	-	-	-	-

*	Indicates a plant waste stream.
-	Test not performed.
SP:	Slightly Positive
P:	Positive
N:	Negative
H:	High toxicity
M:	Medium toxicity (i.e., rats showed hair loss, eye discoloration, etc.)
L:	Low toxicity (i.e., no significant effects noted)

[a] EC-50's were calculated on the XAD-2 extract for the barrel valve vent and separator vent gases by:

$$\text{EC-50} = \begin{bmatrix}\text{EC-50 reported}\\ \text{in ul of extract}\\ \text{per ml culture}\end{bmatrix} \times \begin{bmatrix}\text{mg of organics}\\ \text{extracted per ml}\\ \text{of extract}\end{bmatrix} \times \begin{bmatrix}\text{mg of organics}\\ \text{per Nm}^3\text{ of}\\ \text{vent gas}\end{bmatrix} = \text{Nm}^3 \text{ vent gas/ml culture}$$

(g): gas, (s): solid, (l): liquid

[b] EC-50's and LC-50's for fresh and salt water tests are presented in wt % of the sample in water.

[c] Soil microcosm tests are ranked for No. 1 the most toxic to No. 5 the least toxic.

Source: Environmental Sampling and Analysis Program in a Commercial Low-Btu Gasification Facility - Preliminary Results the MEG category that could be present in the sample and the ratio of estimated concentration to MATE value.

From the example data given in Table 6-1, the following conclusions can be drawn.

- The fused aromatics category (>216 Molecular Weight) had a concentration/MATE ratio much greater than unity; therefore, further characterization of this sample is required.
- Fused aromatics (<216 MW), carboxylic acids, sulfur and heterocyclic sulfur categories have ratios close to unity and may require further characterization.
- For the remaining compound categories, the ratios are much less than one; therefore, further characterization may not be required.

From the above conclusions, further characterization of LC fractions 2 and 3 (containing fused aromatics) is required. This characterization, however, may range between just looking for benzo-a-pyrene to performing a comprehensive GC/MS characterization of all the organic species present in these fractions. A decision to go back to the test site and perform a Level 2 quantitative waste stream characterization test may also be appropriate to characterize the emission rates of specific fused aromatic compounds in the waste stream sampled.

Level 1 Bioassay Tests - Bioassay tests for Level 1 studies can be performed on the total waste stream sample or on certain fractions of the sample (*e.g.*, the extract from the XAD-2 resin used to capture organic species). As discussed in Section 5.0, Analytical Procedures, Level 1 bioassay tests include screening tests for both health and ecological effects. The exact procedures and interpretations of the results from these bioassay tests are currently under development by the EPA.

Bioassay tests have been performed on certain samples collected from a low-Btu gasification facility (as described in Section 3.0). The results of these tests are shown in Table 6-2. The conclusions that can be drawn from these results are listed below.

- The separator liquor sample was very toxic to aquatic species; however, it was least toxic in the soil microcosm test, had negative results for mutagenicity (carcinogenicity), cytotoxicity, and rodent acute toxicity. Because of the toxic effects on aquatic species, this liquor would need to be treated before being discharged into a receiving water body.

- The cyclone dust and tar were the most toxic samples analyzed by the soil microcosm tests and would require treatment if these streams were sent to a landfill.

- The separator tar had a positive Ames test result and was the most toxic sample tested in the rodent acute toxicity tests. Although this stream is not a waste stream, fugitive tar emissions from pumps, valves, etc. could present a hazard to workers in the plant.

- Positive results were obtained from the Ames test on the barrel valve vent gas XAD-2 extract. Therefore, the barrel valve vent gas should be treated before being discharged into the atmosphere.

- The gasifier ash was lowest in soil microcosm toxicity and showed low toxicity signs in the rodent acute toxicity tests. Leachate from the ash should be tested independently; however, these data indicate that disposing of the ash in landfills may be an acceptable control.

From the bioassay test results shown in Table 6-2, it is obvious that not all of the tests give all positive (high toxicity) or negative (low toxicity) results (e.g., the separator liquor is highly toxic to aquatic species but showed negative or low toxicity in the other tests). Therefore, all of these tests are necessary to ensure that a complete biological screening is performed on each sample.

Level 2 Quantitative Test -

The purpose of a Level 2 waste stream characterization test is to provide quantitative data for pollutants in waste streams. These data may be either compound classes or specific compounds, depending upon the objectives of the Level 2 test. For example, quantitative data for classes of compounds may be specified for defined input streams to a needed control device. Quantitative data for specific compounds may be required to determine whether a control device is needed or whether a specific compound needs to be continuously monitored (Level 3).

In order to satisfy the objectives of a Level 2 test, raw chemical data need to be reduced such that the emission rates of pollutants in a waste stream can be determined. The results of the Level 2 characterization program can then be used to answer the following questions.

- Are the pollutant (*e.g.*, NO_x, SO_x) emission rates within environmental standards?
- Will specific pollutants present a potential health and environmental hazard?
- What type of control equipment will be required to treat the waste stream?
- Is continuous monitoring of specific pollutants required?

It should be emphasized that because the objective of Level 2 tests is to obtain quantitative results, data validation techniques, as discussed in Section 6.2, should be used before evaluating those results.

Level 3 Continuous Monitoring Tests -

The purpose of a Level 3 waste stream characterization program is to provide continuous data on the emission rates of specific pollutants in a waste stream. Data reduction and evaluation techniques are similar to those required for Level 2 data to obtain pollutant emission rate information.

6.3.2 Control Equipment Characterization Tests

The purpose of a control equipment characterization test is to obtain information on the effectiveness of a control process in treating a waste stream or to collect data required to design a control process to treat a waste stream. The data obtained from this type of environmental test require evaluation techniques as simple as calculating compound flow rates or as complex as developing an equation for the design of a control process.

An example of the complexity of data evaluation procedures for a control equipment characterization test is to obtain design information for a hot acid gas removal process. The type of design data required include:

- mass flow rates of streams, major compounds, and acid gases to be treated;
- mass flow rates of compounds that may interfere with the removal of acid gases;
- physical conditions (temperature and pressure) of the stream to be treated; and
- kinetic expression for the rate of removal of acid gases as a function of reactant species concentration, temperature, and pressure.

Statistical analysis techniques can also be applied to the results of control equipment characterization tests. Of these techniques, two are particularly important - correlation analysis and regression analysis. Detailed discussions of these statistical techniques are available in the literature (Ref. 67 and 68).

The features of correlation analysis are:

- gives a quantitative assessment of the extent to which two parameters vary together,
- requires only that data for the two parameters be collected in pairs and that they come from a bivariate normal distribution,
- is an excellent means for comparing the results of alternative sampling/analytical procedures, and
- cannot be used to study cause-and-effect relationships between variables.

In comparison, regression analysis:

- provides an estimate of error in the data generation chain,
- provides an estimate of the dependence of one variable on one or more other variables, and
- can be used to develop a simulation model of a process or process module.

6.3.3 Process Stream Characterization Test

The purpose of a process stream characterization test is to provide information on the relationship between process operating parameters and the characteristics of the process waste streams. The data reduction and evaluation procedures required for this test are similar to those for control equipment characterization tests. Mass flow rates and concentrations of pollutants need to be calculated from the raw sampling and analytical data. Process operating parameters (stream flow rates, temperature, pressure) also need to be accurately measured if data are to be obtained for checking or developing a process design equation. As for control equipment characterization tests, statistical analyses often are useful data evaluation techniques for process stream characterization tests.

6.4 DATA HANDLING

The results of an environmental sampling and analysis program will usually comprise an extensive data base. Each piece of analytical data must be correlatable or identifiable with the plant operating conditions at the time of sampling. These data may either be recorded in tabular form and stored under process key words or coded and stored in a computer data base.

6.4.1 Manual Data Base Organization

The key feature of any data storage system is its ability to provide efficient and logical accession of its contents. If the data are organized in a manual retrieval data base, all bits of data should be related to the specific test run in which they were generated and organized under key word subject categories.

Each test run should be given a unique name and reference number. Test run references should then be listed under key word subject categories so that personnel desiring information under one of these topics can quickly identify which test runs are of interest. One way to handle this is to list references to test runs on 3 x 5 library cards.

Of course, referencing test run information through key word categories only provides a list of data sources (unique test run numbers) The actual data must still be available in some convenient and readily accessible form. This could be the final reports on the results of each characterization test run. Pertinent information from each characterization test run can also be summarized on tables and each table given a unique code number. In this case, it would be these numbers which would be listed under the key word categories to guide personnel in accessing characterization data.

Key data subject categories should consist of topics for which it is anticipated that retrieval of data will be desirable. As an example, it would be desirable to access data by process, by control equipment, by streams and their sources, and by pollutants. Suggestions for organizing the data in each of these key word categories are shown in Table 6-3.

Information under the process and control equipment key word categories should include information unique to that process that might separate it from a similar process in another plant, such as feedstock process capacity, operating parameters, input and output streams, and product gas end-use. Information under stream and effluent key words should define the process and site to which the stream data are related: flow rates, pressure, temperature, chemical composition, stream source and

Table 6-3. KEY WORD CATEGORIES FOR ENVIRONMENTAL ASSESSMENT DATA BASE

- **Process Key Words**
  - Coal Pretreatment
    - Drying
    - Partial Oxidation
    - Storage
    - Handling
    - Crushing/sizing
    - Briquetting
    - Pulverizing
  - Coal Gasification
    - Fixed-bed, pressurized, dry ash
    - Entrained-bed, pressurized, slagging
    - Fixed-bed, pressurized, slagging
    - Fixed-bed, atmospheric, dry ash
    - Fluid-bed, atmospherid, dry ash
    - Entrained-bed, atmospheric, slagging
  - Gas Purification
    - Particulate removal
    - Tar removal
    - Quenching and cooling
    - Acid gas removal
- Control Equipment Key Words
  - Air Pollution Control
    - Particulate control
    - Sulfur control
    - Hydrocarbon control
    - Nitrogen oxide control
    - Others (noise, heat, etc.)
  - Water Pollution Control
    - Oil/water separation
    - Suspended solids removal
    - Dissolved organics removal
    - Dissolved inorganics removal
  - Solid Waste Control
    - Chemical fixation
    - Sludge reduction
  - Ultimate Disposal
    - Landfill
    - Evaporation ponds
- Streams and Their Sources
  - Process Streams (Source)
    - Raw product gas (Wellman-Galusha Gasifier)
  - Waste Stream (Source)
    - Coal feeder vent gas (coal feed lock hopper)
- Pollutants (Stream/Source)
  - Sulfur Oxides (flue gas/low-Btu gas boiler)

stream disposition, and any basic plant information which would impact stream flow or composition (coal feed rate and characteristics, unusual plant operating conditions, etc.). Data available under chemical species should be similar to that listed under stream or source names. These data should include the amount or rate of discharge of the chemical species, physical and chemical characteristics of the stream, and information on the effluent source and plant conditions at the time the data were obtained.

All bits of information should reference the environmental test during which the data were gathered. This would allow data to be considered in terms of the time, plant conditions, and any extraneous problems that occurred during that particular characterization effort.

6.4.2 Computer Data Base

A computer data base would be organized similarly to a manual data base and would contain the same information. All bits of characterization data would have to be coded and entered in the computer. Information could then be retrieved by computer output and search commands. The primary advantage of the computer data base is that it could more easily handle the large amounts of information which would be generated in a number of environmental test efforts. Also a computer data base could be adapted for search and comparison routines (*e.g.*, identification of all SO_x sources that exceed a specified level, or identification of sources that contain a certain combination of pollutants and exceed a specified flow rate).

As in the manual data base, all information would have to be linked to the unique environmental test (process, site, and time) and to process conditions and operating mode that provide the basis for the test.

SECTION 7.0

REFERENCES

1. Hamersma, J. W., S. L. Reynolds, and R. F. Maddalone, IERL-RTP Procedures Manual: Level 1 Environmental Assessment. EPA 600/2-76-106a. Redondo Beach, CA, TRW Systems Group, June, 1976.

2. U.S. Department of the Interior, Bureau of Reclamation, Upper Colorado Region, El Paso Gasification Project, San Juan County, NM, draft environmental statement. DES-74-77. 1974.

3. El Paso Natural Gas Company, Application of El Paso Natural Gas Company for a Certificate of Public Convenience and Necessity. Docket No. CP73-131. El Paso, TX, 1973.

4. Environmental Protection Agency, "Sample and Velocity Traverses for Stationary Sources, 40 CFR 60, App. A, Reference Method 1," Fed. Reg. 41(111), 23061-63, (1976).

5. National Institute for Occupational Safety and Health, Public Health Service, The Industrial Environment - Its Evaluation and Control. Contract No. HSM-99-71-45, Washington, DC, GPO, 1973.

6. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants, Revised. Cincinnati, OH, April 1977.

7. Ames, Bruce N., et. al., "Carcinogens as Frameshift Mutagens: Metabolites and Derivatives of 2-Acetylaminofluorene and Other Aromatic Amine Carcinogens," Proc. Nat. Acad. Sci. 69(11), 3128-32 (1972).

8. Ames, Bruce N., Frank D. Lee, and William E. Durston, "An Improved Bacterial Test System for the Detection and Classification of Mutagens and Carcinogens," Proc. Nat. Acad. Sci. 70(3), 782-86 (1973).

9. Ames, Bruce N., at al., "Carcinogens are Mutagens: A Simple Test System Combining Liver Homogenates for Activation and Bacteria for Detection," Proc. Nat. Acad. Sci. 70(8), 2281-85 (1973).

10. Luthy, Richard G., Manual of Methods: Preservation and Analysis of Coal Gasification Wastewaters. FE-2496-8. Pittsburgh, PA, Carnegie-Mellon University Environmental Studies Institute, July 1977.

11. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes. EPA 625 /6-74-003. Washington, DC, Environmental Protection Agency, Office of Technology Transfer, 1974.

12. Harstein, A. M., R. W. Freedman, and D. W. Platter, "Novel Wet-Digestion Procedures for Trace-Metal Analysis of Coal by Atomic Absorption," Anal. Chem. 45(3), 611 (1973).

13. American Public Health Association, American Water Works Association, and Water Pollution Control Federation, Standard Methods for the Examination of Water and Waste Water, 14th ed. Washington, DC, American Public Health Association, 1975.

14. American Society for Testing and Materials, 1977 Annual Book of ATSM Standards, Part 31, Water. Philadelphia, PA, 1977.

15. Oldham, Ronald G., and Robert G. Wetherold, Assessment, Selection, and Development of Procedures for Determining the Environmental Acceptability of Synthetic Fuel Plants Based on Coal, Revised Report, 4 vols. FE-1795-3. Austin, TX, Radian Corp., May 1977.

16. Pinta, Maurice, Detection and Determination of Trace Elements. Absorption Spectrophotometry, Emission Spectroscopy and Polarography, Trans. by Miriam Bivas. London, Ann Arbor, 1972.

17. Ruch, Walter E., Quantitative Analysis of Gaseous Pollutants. Ann Arbor, MI, Interscience, 1970.

18. Bailey, J. B. W., N. E. Brown, and C. V. Phillips, "A Method for the Determination of Carbon Monoxide, Carbon Dioxide, Carbonyl Sulphide, Oxygen, and Nitrogen in Furnace Gas Atmospheres by Gas Chromatography," Analyst (London) 96, 477 (1971).

19. Jones, Carolyn N., "Gas Chromatographic Determination of Hydrogen, Oxygen, Nitrogen, Carbon Monoxide, Carbon Dioxide, Hydrogen Sulfide, Ammonia, Water, and C_1 Through C_2 Saturated Hydrocarbons in Refinery Gases," Anal. Chem. 39(14), 1858-60 (1967).

20. Kim, Ann G., and Louise J. Douglas, Gas Chromatographic Method for Analyzing Gases Associated with Coal. R.I. 7903. Pittsburgh, PA, Pittsburgh Mining and Safety Research Center, 1974.

21. Black, Francis M., and John E. Sigsby, "Chemiluminescent Method for NO and NO_x ($NO + NO_2$) Analysis," Environ. Sci. Tech. 8(2), 149 (1974).

22. Baker, R.L., "Determination of Fluoride in Vegetation Using the Specific Ion Electrode," Anal. Chem. 44(7), 1326 (1972).

23. Orion Research Inc., Analytical Methods Guide, 3rd ed. Cambridge, MA, 1972.

24. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry. Norwalk, CT, 1973.

25. Jacobs, M. L., Sandra L. Sweeney, and Clyde L. Webster, "Determination of Trace Elements in Coal by Spark Source Mass Spectrography," Reprint. Keystone Coal Industry Manual. New York, NY, McGraw-Hill, 1975.

26. Ediger, Richard D., "Atomic Absorption Analysis with the Graphite Furnace Using Matrix Modification," Atomic Absorption Newsletter 14(5), 127 (1975).

27. Instrumentation Laboratory, Inc., Analytical Instrument Division, Atomic Absorption Methods Manual, Vol. 2, Flameless Operations. December 1976.

28. Mair, James W., Jr. and Harry G. Day, "Curcumin Method for Spectrophotometric Determination of Boron Extracted From Radio-Frequency Ashed Animal Tissues Using 2-Ethyl-1, 3-Hexanediol," Anal. Chem. 44(12), 3015 (1972).

29. Kinrade, John D., and Jon C. Van Loon, "Solvent Extraction for Use with Flame Atomic Absorption Spectrometry," Anal. Chem. 46(13), 1894-8 (1974).

30. Hoog, Han, "Future Trends in Refining," World Petrol. 1968 (June).

31. Levesque, M., and E. D. Vendette, "Selenium Determination in Soil and Plant Materials," Can. J. Soil Sci. 51, 85-93 (1971).

32. Rankin, John M., "Fluorometric Determination of Selenium in Water w/2,3-Diaminonaphthalene," Environ. Sci. Tech. 7(9), 823 (1973).

33. (G. K.) Turner Associates, "The Fluorometric Determination of Selenium: A Literature Review," Fluorometry Reviews, Acc. No. 11863. Palo Alto, CA, September 1972.

34. Rader, L. F., and F. S. Grimaldi, Chemical Analysis for Selected Minor Elements in Pierre Shale. U.S.G.S. Professional Paper 391-A. Washington, DC, GPO, 1961.

35. (G. K.) Turner Associates, "Uranium," Fluorometry Reviews Series. Palo Alto, CA, February 1968.

36. Cioni, R., F. Innocenti, and R. Mazzuoli, "The Determination of Vanadium in Silicate Rocks with the HGA-70 Graphite Furnace," Atomic Absorption Newsletter 11(5), 102 (1972).

37. American Society for Testing and Materials, 1974 Annual Book of ASTM Standards. Pt. 26, Gaseous Fuels; Coal and Coke; Atmospheric Analysis. Philadelphia, PA, 1974.

38. Burke, Keith E., "Determination of Microgram Amounts of Antimony, Bismuth, Lead and Tin in Aluminum, Iron and Nickel-Base Alloys by Non-Aqueous Atomic-Absorption Spectroscopy," Analyst 97, 19-28 (1972).

39. Bokowski, D. L., "Rapid Determination of Beryllium by a Direct-Reading Atomic Absorption Spectrophotometer," Amer. Ind. Hyg. Assoc. J. 29(5), 474-81 (1968).

40. Carlson, R. M., and J. L. Paul, "Potentiometric Determination of Boron as Tetrafluoroborate," Anal. Chem. 40(8), 1292 (1968).

41. Orion Research Inc., Analytical Methods Guide, 3rd ed. Cambridge, MA, 1972.

42. Thomas, Josephus, Jr., and Harold J. Gluoskoter, "Determination of Fluoride in Coal With the Fluoride Ion-Selective Electrode," Anal. Chem. 46 (9), 1321 (1974).

43. Kalb, G., and Charles Baldeck, The Development of the Gold Amalgamation Sampling and Analytical Procedure for Investigation of Mercury in Stack Gases. PB-210 817. Columbus, OH, TraDet, Inc., 1972.

44. Diehl, R. C. et al., Fate of Trace Mercury in the Combustion of Coal. TPR-54. Pittsburgh, PA, Pittsburgh Energy Research Center, 1972.

45. O'Gorman, J. V., N. H. Suhr, and P. L. Walker, Jr., "The Determination of Mercury in Some American Coals," Applied Spectroscopy 26(1), 44 (1972).

46. Kim, C. H., C. M. Owens, and L. E. Smyth, "Determination of Traces of Mo in Soils and Geological Materials by Solvent Extraction of the Molybdenum-Thiocyanate Complex and Atomic Absorption," *Talanta* *21*, 445-54 (1974).

47. Levesque, M., and E. D. Vendette, "Selenium Determination in Soil and Plant Materials," *Can. J. Soil Sci*. *51*, 85-93 (1971).

48. Jacobs, Morris B., *The Analytical Toxicology of Industrial Inorganic Poisons*. New York, NY, Interscience, 1967.

49. Monteriolo, S. Cerquiglini, and A. Pepe, "Comparative Study of Methods for the Determination of Airborne Fluorides," *Pure Appl. Chem*. *24*(4), 707-14 (1970).

50. Headridge, J. B., and D. Risson Smith, "Determination of Trace Amounts of Antimony in Mild Steels by Solvent Extraction Followed by Atomic Absorption Spectrophotometry," *Lab. Practice* *20*(4), 312 (1971).

51. Boar, P. L., and L. K. Ingram, "The Comprehensive Analysis of Coal Ash and Silicate Rocks by Atomic-Absorption Spectrophotometry by a Fusion Technique," *Analyst* *95*, 124-30 (1970).

52. Spindt, R. S., First Annual Report on Polynuclear Aromatic *Content of Heavy Duty Diesel Engine Exhaust Gases, For Period Ending 1 July 1974*. PB-238 688. Pittsburgh, PA, Gulf Research and Development Company, 1974.

53. Kleopfer, Robert D., and Billy J. Fairless, "Characterization of Organic Components in a Municipal Water Supply," *Environ. Sci. Tech*. *6*(12), 1036-37 (1972).

54. Hughes, D. R., R. S. Belcher, and E. J. O'Brien, "A Modified Extraction Method for Determination of Mineral Oil in Sea Water," *Bull. Environ. Contam. Toxicol*. *10*(3), 170 (1973).

55. Pierce, Ronald C., and Morris Katz, "Dependency of Polynuclear Aromatic Hydrocarbon Content on Size Distribution of Atmospheric Aerosols," *Environ. Sci. Tech*. *9*(4), 347 (1975).

56. Webb, Ronald G., et al., *Current Practice in GC-MS Analysis of Organics in Water*. EPA-R2-73-277. Athens, GA, EPA, Southeast Environmental Research Lab., 1973.

57. Happel, John, Robert E. Lief, and Reiji Mezaki, "A Theoretical Model Suitable for Higher Conversion Data of Sulfur Dioxide Oxidation," *J. Catalysis* *31*, 90-95 (1973).

58. Jewell, D. M., et al., "Ion-Exchange, Coordination, and Absorption Chromatographic Separation of Heavy End Petroleum Distillates and the Analysis of Hydrocarbon Fractions," ACS, Div. Pet. Chem., Prepr. 16(4), C13-20 (1971).

59. Fiegel, F., Spot Tests in Organic Analysis, 7th ed. New York, NY, Elsevier, 1966.

60. Farrar, T. C., and E. D. Becker, Pulse and Fourier Transform NMR. New York, NY, Academic Press, 1971.

61. Keith, Lawrence H., ed., Identification and Analysis of Organic Pollutants in Water. Ann Arbor, MI, Ann Arbor Science, 1976.

62. McFadden, William, Techniques of Combined Gas Chromatography/ Mass Spectrometry. New York, NY, Wiley, 1973.

63. Cochran, William G., and Gertrude M. Cox, Experimental Designs, 2nd ed. New York, NY, Wiley, 1957.

64. Perry, John H., Chemical Engineers Handbook, 5th ed. New York, NY, McGraw-Hill, 1973.

65. Conner, W. S., and Marvin Zelen, Fractional Factorial Experimental Designs for Factors at Three Levels. Applied Mathematic Series 54. Washington, DC, NBS (GPO), 1959.

66. Deming, Lois S., Fractional Factorial Experimental Design for Experiments at Two Levels. Applied Mathematics Series 48. Washington, DC, NBS (GPO), 1957.

67. Snedecor, G. W., and W. C. Cochran, Statistical Methods, 6th ed. Ames, IA, Iowa State University Press, 1967.

68. Bowker, A. H., and G. J. Lieberman, Engineering Statistics. Englewood Cliffs, NJ, Prentice-Hall, 1960.

69. Ryan, L. E., R G. Beimer, and R. F. Maddalone, Approach to Level 2 Analysis Based on Level 1 Results, MEG Categories and Compounds and Decision Criteria. Redondo Beach, CA, TRW, 12 January 1978.

70. Harris, Judith C., Suggested Report Format for Level 1 Organic Analysis Data. Cambridge, MA, Arthur D. Little, Inc., 21 October 1977.

71. Cleland, J. G. and G. L. Kingsbury, Multimedia Environmental Goals for Environmental Assessment, Vol. 1, Final Report. EPA-600/7-77-136A, Research Triangle Park, NC, Research Triangle Institute, November 1977.

APPENDIX

SAMPLING METHODS

In this appendix the approaches and techniques for collecting samples from three major stream types (gas, liquid and solid) are presented. Sampling procedures for collecting samples containing mixtures of these phases are discussed under the section dealing with the major stream phase. For example, particulate matter entrained in a gas stream is discussed in the gas sampling section. Liquid-solid slurries are discussed in the liquid sampling section.

A-1 GAS SAMPLING

The selection of sampling techniques for collecting gas samples requires a knowledge of the following:

- stream physical conditions (temperature, pressure, particulate and condensable content, etc.),
- major chemical components in the stream,
- reactivity of stream components relating to both sample stability and safety considerations, and
- physical arrangement of the piping or ducting containing the stream.

This information is available from the analysis of the test site.

The primary emphasis of the following sections is on manual methods for collecting gas samples, since the decision to employ continuous monitoring is often based on the results of these methods. Execution of either approach requires:

- a carefully selected sampling point, and
- access to the stream and withdrawal of a portion of that stream with immediate or delayed analysis. (Some continuous techniques avoid the withdrawal of gas from the stream by analysis "in situ.")

Selection of the proper sampling point is discussed in Section 4.0 The following text contains a discussion for sampling train selection (sample withdrawal system) and continuous monitoring techniques. Also discussed are techniques for collecting fugitive gas samples from valves, flanges, etc. in a coal gasification facility.

A-1.1 Sampling Train

The sampling train, or system of collection devices, performs several functions, each of which must be considered in selecting a suitable train. These functions are to:

- transport a portion of the gas stream to the collection (and conditioning) sections,
- provide a controlled interface between the gas stream and the plant work environment,
- condition the sampled gas as required for the collection sections,
- collect the components of interest,
- measure the volume of gas sampled, and
- measure stream conditions (temperature, pressure, flow rate).

The sampling train designed to fulfill these functions consists of four sequential sample-processing units. These are:

- probe assembly,
- particulate collection unit,

- vapor collection unit, and
- metering unit.

Through various combinations of its individual components, this general-purpose sampling train is used to characterize a wide range of analytical parameters. The sampling involves removing the gas sample from the stream over a specified period of time. The train concept presented here is based upon the EPA's Method 5 for characterizing particulate matter in gas streams (Ref. A-1). This concept can also be applied to the Source Assessment Sampling System (SASS) developed for Level 1 waste stream characterization tests. The Method 5 and SASS trains are illustrated in Figures A-1 and A-2.

Systems of this general type are available commercially and are suitable for a variety of applications. Gas stream temperature and pressure and the specific requirements of the parameters analyzed may dictate modifications. The following sections discuss each unit of the train, its limitations, and many of the possible options for modification.

A-1.1.1 Probe Assembly

The probe assembly performs several discrete functions, each of which must be considered in its design or selection. These functions are to:

- provide sample removal from the stream at a point or series of points (traversing) to give a representative sample,
- provide a controlled interface between stream and environment (particularly important for pressurized or toxic streams),
- transport the sampled gas to the remainder of the train without contamination or alteration of composition, and
- provide measurement of stream velocity (flow rate), temperature and pressure, as required.

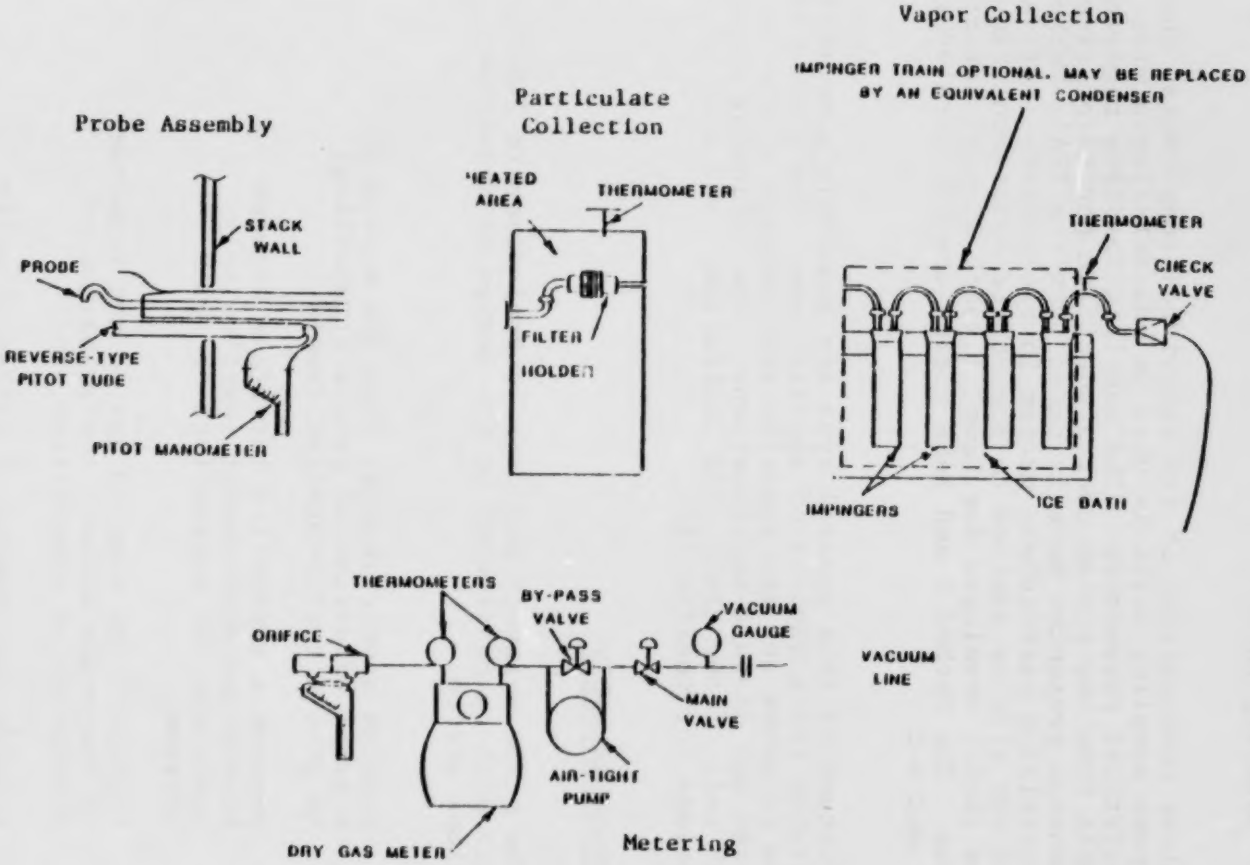
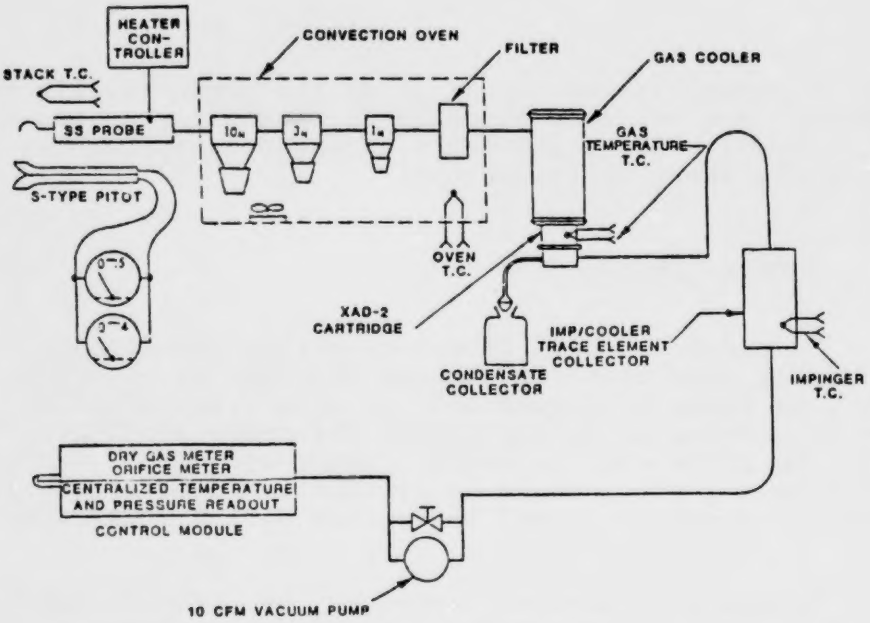
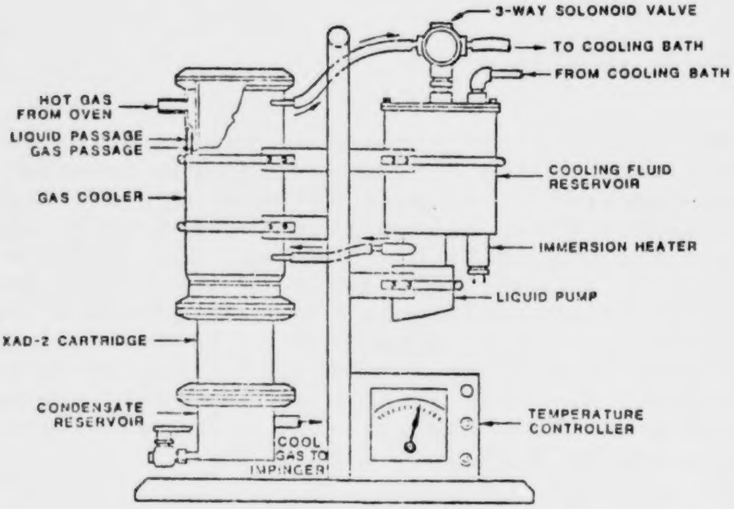

Probe Assembly
Particulate Collection
Vapor Collection
IMPINGER TRAIN OPTIONAL. MAY BE REPLACED BY AN EQUIVALENT CONDENSER
STACK WALL
PROBE
REVERSE-TYPE PITOT TUBE
PITOT MANOMETER
HEATED AREA
THERMOMETER
FILTER HOLDER
THERMOMETER
CHECK VALVE
IMPINGERS
ICE BATH
THERMOMETERS
BY-PASS VALVE
VACUUM GAUGE
ORIFICE
VACUUM LINE
MAIN VALVE
AIR-TIGHT PUMP
DRY GAS METER
Metering

Figure A-1. EPA 5 SAMPLING TRAIN


HEATER CON- TROLLER
CONVECTION OVEN
FILTER
GAS COOLER
STACK T.C.
SS PROBE
10μ
3μ
1μ
GAS TEMPERATURE T.C.
S-TYPE PITOT
OVEN T.C.
XAD-2 CARTRIDGE
IMP/COOLER TRACE ELEMENT COLLECTOR
CONDENSATE COLLECTOR
IMPINGER T.C.
DRY GAS METER
ORIFICE METER
CENTRALIZED TEMPERATURE
AND PRESSURE READOUT
CONTROL MODULE
10 CFM VACUUM PUMP

SOURCE ASSESSMENT SAMPLING SCHEMATIC


3-WAY SOLONOID VALVE
TO COOLING BATH
FROM COOLING BATH
HOT GAS FROM OVEN
LIQUID PASSAGE
GAS PASSAGE
GAS COOLER
COOLING FLUID RESERVOIR
IMMERSION HEATER
LIQUID PUMP
XAD-2 CARTRIDGE
CONDENSATE RESERVOIR
COOL GAS TO IMPINGER
TEMPERATURE CONTROLLER

XAD-2 SORBENT TRAP MODULE

Figure A-2. COLLECTION OF ADSORBABLES WITH SASS TRAIN

A probe assembly consists of the probe itself, the outer jacket, and selected elements for measuring stream conditions. Examples for right-angle and head-on approaches to the stream are shown in Figure A-3.

Sample Removal -

To provide access to points within the stream, the probe assembly must protrude through the duct or pipe wall either "head on", as shown in Figure A-4, or at a right angle to it. To allow traversing of points within the cross-sectional of the gas line, the probe must be mobile during operation, and more than one sampling port should be available. Sample port locations are discussed in detail in Section 4.0 of this report.

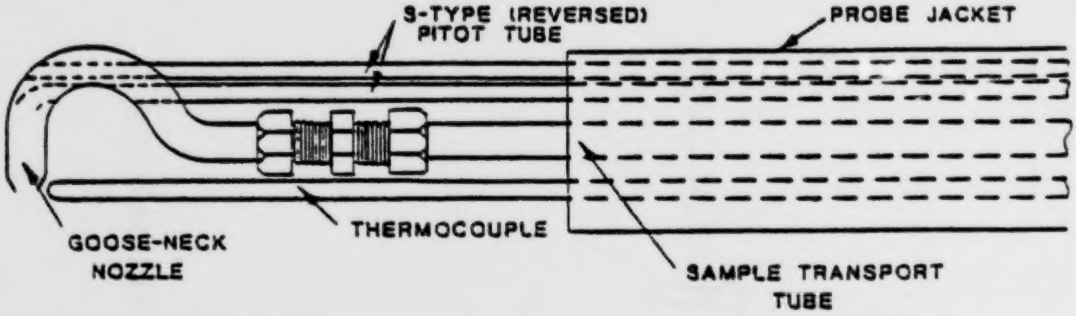
Permanently mounted probes may be used if sampling at several points is required. For streams containing high levels of particulates or condensable tars, the use of permanently mounted probes is not advisable due to potential probe plugging problems. Removable probes should be used to allow cleaning or replacement.

Probe Interface -

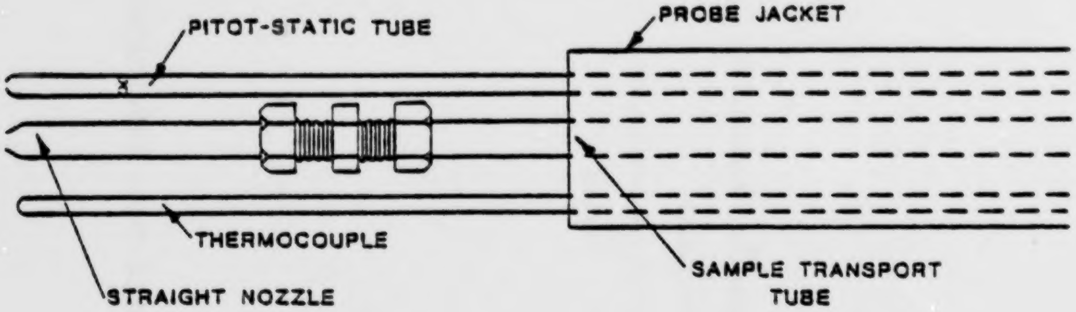
For nontoxic gas streams at pressures close to atmospheric, the design of the stream-environment interface is not particularly important. A loose fitting cap, or stuffing around the probe assembly which allows it to move freely, will suffice. The interface becomes critical, however, for toxic or pressurized streams demanding a leak-tight seal. A lubricated packing gland similar to valve-stem packing is the most generally applicable option. Figure A-5 illustrates such an interface. The packing gland is mounted on a fully opened gate valve or ball valve of adequate internal diameter (3-inch is generally adequate) to allow insertion of the probe assembly. The valve provides closure of the sampling port when not in use.

Gas Transport -

The probe's primary function is collecting and transporting the sample without contamination or alteration. The nozzle and sample-transport tube must be constructed of inert


S-TYPE (REVERSED) PITOT TUBE
PROBE JACKET
GOOSE-NECK NOZZLE
THERMOCOUPLE
SAMPLE TRANSPORT TUBE

PROBE DESIGN FOR 'RIGHT ANGLE' SAMPLING


PITOT-STATIC TUBE
PROBE JACKET
THERMOCOUPLE
STRAIGHT NOZZLE
SAMPLE TRANSPORT TUBE

PROBE DESIGN FOR 'HEAD-ON' SAMPLING

Figure A-3. SAMPLING PROBE ASSEMBLIES

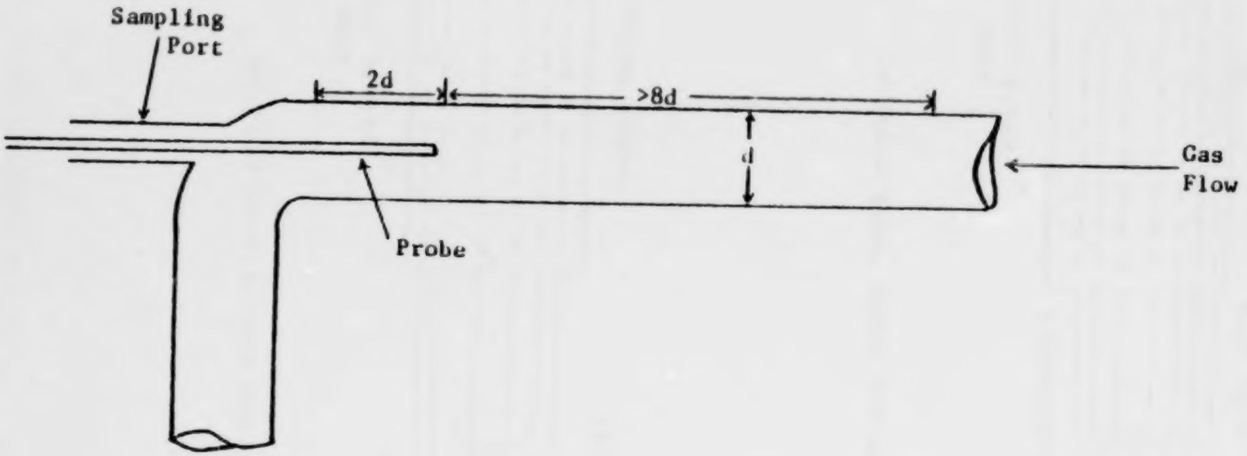

Sampling
Port
2d
>8d
d
Gas
Flow
Probe

Figure A-4. SAMPLE PORT ARRANGEMENT FOR "HEAD-ON" PROBES SAMPLING

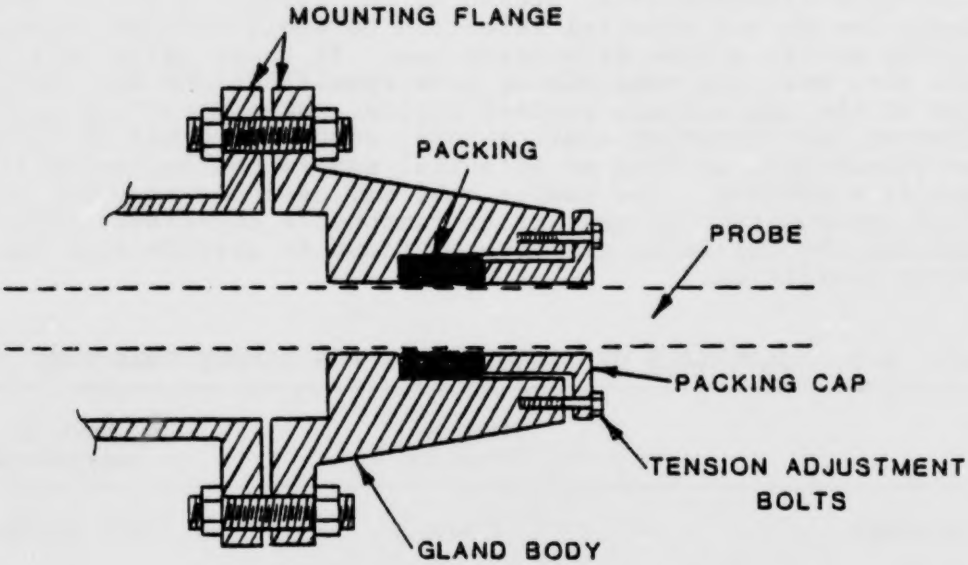

MOUNTING FLANGE
PACKING
PROBE
PACKING CAP
TENSION ADJUSTMENT BOLTS
GLAND BODY

Figure A-5. PACKING GLAND ASSEMBLY CUT-AWAY DIAGRAM material to avoid contamination or reaction with the tube walls. The EPA Method 5 train mentioned earlier accomplishes this with a pyrex glass probe liner. This serves very well for applications where temperature and pressure limitations of the glass are not exceeded.

Table A-1 summarizes some of the possible materials for transport-tube construction and their limitations. Extreme conditions (temperatures, pressures, or corrosive gases) require expert design and material selection to avoid contamination from scaling and to ensure safe operation. In these cases, the equipment must meet the same piping code specifications for construction as the appropriate process piping. When materials are selected for corrosive applications, compromises may be made for short-term use, as long as potential sample contamination is kept at a minimum. The sample tube may need heat tracing to avoid condensation of gas stream components especially when sampling the tar-laden gas streams found in certain coal gasification facilities.

Table A-1. MATERIALS OF CONSTRUCTION FOR SAMPLE TRANSPORT TUBES

	Maximum Pressure	Maximum Temperature
Pyrex Glass	2 psig	770°K (930°F)
Quartz	2 psig	1370°K (2010°F)
Teflon	50 psig*	500°K (440°F)
Stainless Steel (304 or 316 Series)	*	820°K (1020°F)
Inconel 600 Series	*	1170°K (1650°F)

* Dependent on wall thickness and construction

The nozzle at the collecting end of the sample-transport tube should be constructed of the same material as the transport tube. This is not always a rigid requirement, since the sampled gas is exposed to the nozzle for only a small fraction of the transport time. Interchangeable nozzles of varying internal diameters are necessary to meet the requirements of isokinetic sampling and remain within the flow-rate limitations of the sampling train. Isokinetic sampling (when the sample flow velocity equals that of the stream) is discussed in the section on particulate collection. To minimize turbulence, the nozzle edges must be tapered as sharply as possible.

Sample Measurement -

The final function of the probe assembly is to measure the stream's temperature, pressure, and flow rate. The designs shown in Figure A-3 include thermocouples and pitot tubes for doing this. Thermocouples with sheathing material selected for stream conditions are recommended for their increased durability and reliability. Two types of pitots are in common use, S-type (reversed) and pitot-static. The function of each is to determine the velocity of the gas by measuring the pressure differential between the velocity head and the stream static head (S-type differential includes a negative pressure effect produced by the eddy effect on the downstream side). For each type, the following equation relates the differential pressure to the gas velocity:

$$V_s = 85.48\ C_p \left[\frac{T_s(P_p - P_w)}{P_s M} \right]^{\frac{1}{2}} \qquad \text{(A-1)}$$

where

V_s = gas velocity (feet per second),

P_w = measured static pressure (inches of water),

P_p = measured total pressure (inches of water),

$P_p - P_w$ = measured differential pressure (inches of water),

C_p = pitot coefficient (1.00 for pitot-static, ∿0.85 for S-type; but it should be determined by calibration),

T_s = stream temperature (°R),

P_s = absolute stream pressure (inches of Hg), and

M = gas molecular weight (wet basis).

The static pressure of the gas stream is measured on the static leg of the pitot-static or, if an S-type pitot is used, by rotating the probe so that the pitot is oriented at a right angle to the flow and measuring the pressure on either leg, with the other leg disconnected.

A-1.1.2 Particulate Collection Unit

Particulate matter entrained in a gas stream is collected for one or more of four possible objectives. Aside from the obvious one of providing particulate-free gas for the vapor-collection unit, three common functions for providing information about the nature of the particulate matter in a gas stream are:

- measuring particulate loading in the stream,
- determining particulate size distribution, and
- determining particulate composition.

For all three functions, compositing and isokinetic sampling techniques are required.

Compositing -

Particulate material is not necessarily distributed evenly throughout the gas stream. Such maldistribution requires traversing of the sample points within the sampling plane, as discussed in Section 4.0, to collect a representative sample. The traversing may consist of individual samples (or determinations) for each point, or else a composite sample created by particulate collection at each point for an equal time period.

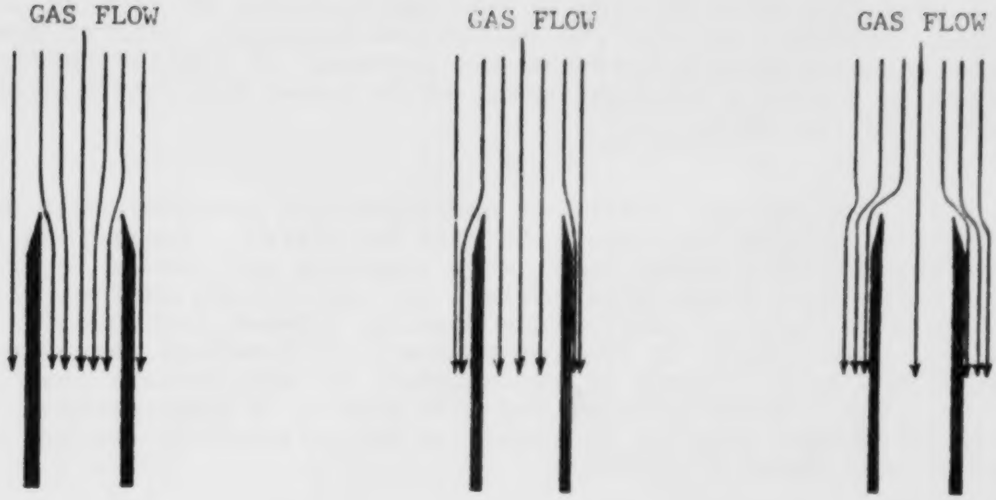
Isokinetic Sampling -

Isokinetic sampling requires that the sampled gas stream enter the probe nozzle at the same velocity as the gas stream velocity. Deviation from this requirement will result in a size separation of particulates at the nozzle tip due to the momentum of the larger particles. The gas flow patterns for isokinetic rates and deviations from those rates are illustrated in exaggerated fashion in Figure A-6. Small particulates will follow the gas flow patterns shown while larger particulates will follow a straight path relatively independent of gas flow patterns. These two extremes of behavior will be exhibited over the entire size distribution of the particulates in varying degrees, depending on the gas velocities involved. Higher gas-stream velocities will increase the tendency of smaller particulates to follow a straight path, while lower velocities will reduce this tendency.

The obvious result of nonisokinetic sampling will be that measured size distributions will be biased: toward smaller size ranges during super-isokinetic sampling and toward larger size ranges during sub-isokinetic. Not so obvious is the effect on determinations of particulate loading. Super-isokinetic sampling will result in lighter-than-actual loadings, because some of the particulates in the sampled gas will bypass the nozzle. Sub-isokinetic sampling will result in heavier-than-actual loadings, because particulates not already in the gas sampled will enter the nozzle.

Even less obvious is the effect of nonisokinetic sampling on particulate composition. The composition of particulates is rarely independent of particle size, so a shift in the representation of size distribution is likely to result in a compositionally unrepresentative sample. Deviations of the sampling rate within 10 percent on either side of isokinetic will not significantly affect the results.

The Method 5 train (Figure A-1) collects entrained particulates with the passage of the gas sampled from the probe to a filter mounted in an oven maintained at 380°K (225°F). The EPA specification of a collection temperature in this procedure effectively defines what material is considered to be particulate matter. In this case, materials which condense above 380°K (225°F) are included and those which remain vaporous at 380°K (225°F) are excluded.


GAS FLOW
GAS FLOW
GAS FLOW

SUPER-ISOKINETIC **ISOKINETIC** **SUB-ISOKINETIC**

Figure A-6. NOZZLE GAS FLOW PATTERNS ILLUSTRATING ISOKINETIC SAMPLING

The selection of the collection temperature must, therefore, be made in light of test objectives (*e.g.*, regulatory requirements require collection at a specified temperature) and stream composition. If the primary test objective is determining the actual stream particulate content, then collection at stream conditions is recommended. One approach which inherently requires collection at stream conditions includes mounting the particulate collection device on the end of the probe extended physically into the gas stream. This has the added advantage of avoiding losses of material to the transport-tube walls.

If collection outside the stream is chosen, the sample-transport tube must be designed to minimize losses. This is accomplished primarily by providing smooth flow contours that avoid protrusions or sharp directional changes in flow and by heating the transport tube to avoid condensation. Particulates entrained in pressurized gas streams should be collected at stream pressure to avoid losses of material during passage through a pressure-reduction step. Since some probe losses are inevitable, the material must be recovered by washing the transport tube with a suitable solvent (Method 5 specifies acetone) following completion of any collection.

The specific collecting devices selected for the particulate-collection unit depend upon the techniques found effective for the primary purpose of the particulate collection - whether for loading, size distribution, or composition.

Particulate Loading -

The common basis for all particulate-loading measurements is the particulate weight per unit volume of gas. The determination of particulate loading in a gas stream involves collecting all particulate material from a portion of the stream, determining the weight of collected material, and dividing the particulate weight by the total volume of gas sampled.

The particulate-loading procedures differ only in their collection technique. EPA's Method 5 specifies an all-glass system with a glass-fiber filter and a glass cyclone (for heavy loadings), both mounted in an oven maintained at 380°K (225°F). The ASME Power Test Code specifies an alundum thimble-type filter located in the main gas stream (Ref. A-2). A modification of this ASME procedure uses a 47 mm glass-fiber filter, also in the gas stream. The particulate collection technique for the SASS train is a series of three cyclones followed by a glass fiber filter.

Modifications of these procedures for special applications, or for accommodating gas stream conditions, are perfectly valid if designed with the restrictions of the above discussion taken into consideration. For example, a particulate collection unit designed to determine the collection efficiency of a high-temperature cyclone operated under pressure, might include these four elements: a probe assembly with packing gland and gate valve at the interface, a sample-transport tube constructed of Type 316 stainless steel and heat traced to maintain process temperature, a filter holder containing an alundum filter maintained at process temperature and pressure, and a pressure-reducing and flow control valve at the filter exit. This system would provide a measure of the actual stream particulate loading, excluding any material not condensable at process temperature.

Special Considerations -

There are certain types of streams that are unique to coal conversion processes, and therefore, require special sampling techniques. An example of these types of streams is hot product gas (810-1480°K, 100-2200°F) containing high concentrations of entrained particulates, tars and oils. To obtain a representative gas sample from a "hot" stream having high levels of entrained particulates, tars and oils, a sample pretreatment train must be used. This train should remove the particulates, tars and oils in a manner such that the concentrations of the gaseous species are not changed. An example of such a pretreatment train consists of an in-line filter, a knock-out pot, an inert filter, a permeation drier, a pump, and a flowmeter. Bags or sample bombs can then be used to collect the gases for analysis. A schematic of this train is shown in Figure A-7.

Particule Size Distribution -

The most commonly used sampling device for the determination of particulate size distribution is the cascade impactor, shown schematically in Figure A-8. Several vendors manufacture devices which, although different in design, operate

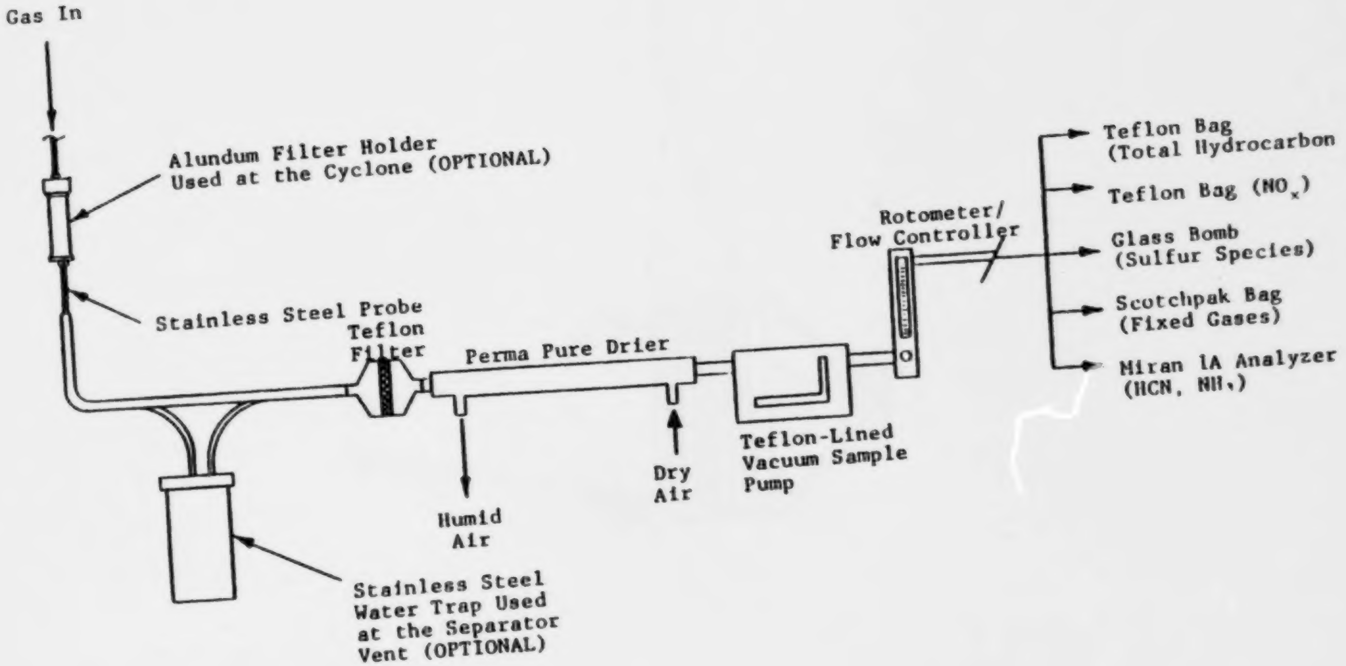

Gas In
Alundum Filter Holder Used at the Cyclone (OPTIONAL)
Stainless Steel Probe
Teflon Filter
Perma Pure Drier
Humid Air
Dry Air
Stainless Steel Water Trap Used at the Separator Vent (OPTIONAL)
Teflon-Lined Vacuum Sample Pump
Rotometer/ Flow Controller
Teflon Bag (Total Hydrocarbon
Teflon Bag (NO_x)
Glass Bomb (Sulfur Species)
Scotchpak Bag (Fixed Gases)
Miran 1A Analyzer (HCN, NH_3)

Figure A-7. GRAB SAMPLE COLLECTION AND PREPARATION SYSTEM

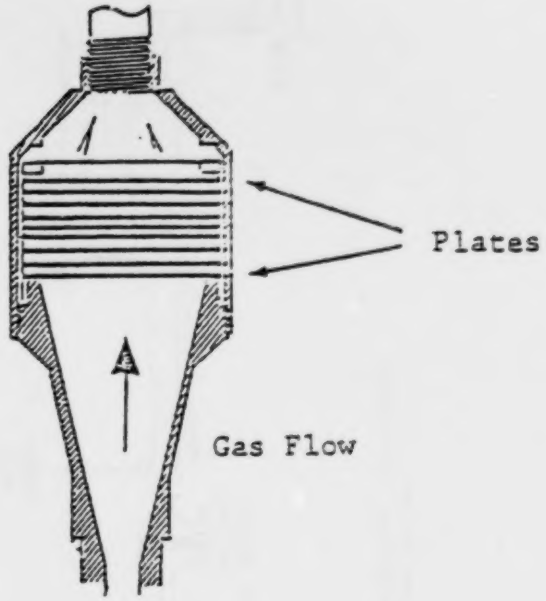

Plates
Gas Flow

Figure A-8. CASCADE IMPACTOR

on the same basic principle. The sample gas stream passes through a series of stages, each of which accelerates the stream to a higher velocity. The increased velocities impart increased momentums to the entrained particulates, which results in successively smaller particulates being collected by impaction on the collection surface.

Some designs make provision for the use of removable substrates of metal foil, polycarbonate, or glass filter media for the collection surface. Others simply use a clean metal surface or plate, which may be coated with a film of grease to reduce "bounce-off" and reentrainment. For each stage, the sizing specifications are dependent on sampling rate, temperature, particle density and gas density according to relationships supplied by the device's manufacturer. A cascade impactor sizes not as a function of physical size but as a function of effective aerodynamic size, which is dependent on physical size, density, and shape. Due to material losses within this device, the sum of the material collected on the individual stages cannot be used to calculate an accurate measure of the total particulate loading.

Particulate Composition -

The objective of particulate collection when determining compositon is to provide the analyst with material representing the composition of the particulates entrained in the gas stream. Three alternative devices deserve consideration, depending on the problem at hand: filters, wet electrostatic precipitators (WEP), and cyclones.

Filtration is the most generally applicable technique for this purpose. The filter medium must be selected to contribute the minimum background for the parameters of interest and to be unreactive with the gas stream or the collected particulate sample. To minimize the influence of the filter on particular analytical parameters, pretreatment of the filter substrates is often required. Gaseous components of the stream samples may react with, or sorb on, the filter medium to produce interferences in subsequent analyses. For example, studies have shown that sorption of sulfur dioxide on filter media, followed by oxidation, is a significant interference in determining sulfates. Many filter configurations are limited in sampling capacity. The alundum thimble filter assembly specified by ASME can provide increased sample quantities over other arrangements available.

Using the wet electrostatic precipitator (WEP) system, shown in Figure A-9, can avoid many drawbacks present in filtration collection. This system is particularly useful in collecting material for elemental analysis. In entering the WEP, the sample gas bubbles through the electrolyte reservoir. The electrolyte is a 5% solution of nitric acid. The gas then passes through the WEP body, where electrostatic collection is induced by a d-c potential of 12 kv between the suspended platinum electrode and the electrolyte-wetted wall. Collected material is washed from the wall by the electrolyte, which is circulated by a peristaltic pump. This system overcomes the sample quantity and interference limitations of filtration collection; however, it simultaneously collects both particulates and vapor-phase elements, which may be a disadvantage in some situations. The WEP is almost as efficient as filtration collection, having at least 99% of the latter's collection efficiency.

For determination of compositon by size fractions, cyclones may be selected for collection. Specially designed sets of cyclones provide controlled fractionation. Each set consists of a series of cyclones designed with progressively smaller effective cutoff diameters so that the material collected in each provides a sample sized between the effective cutoff of the collection cyclone and of the preceding one. The fine particulates escaping the last cyclone may be collected by either filtration or the WEP method. The High Volume Source Assessment Sampling System proposed by EPA for general environmental assessment includes a set of cyclones with effective cutoffs of 14µ, 3µ, and 1µ. To ensure the collection of adequate material in each size range, the approximate particle-size distribution in the gas stream should be known so that a set of cyclones with appropriate cut-offs may be used. The actual size distribution of each collected fraction should be determined by microscopy following collection, since many effects - such as particle agglomeration, wall losses, and electrostatic collection - may cause non-ideal operation of the cyclones. The mass of material collected in the cyclones and its distribution among the various size fractions should be considered mainly for composition; it is only a rough indication of particulate loading or of particle size distribution.

A-1.1.3 Vapor-Collection Unit

The particulate-collection section provides a particulate-free gas stream which is, generally, suitable for the determination of vaporous components and fixed gases. Two precautions

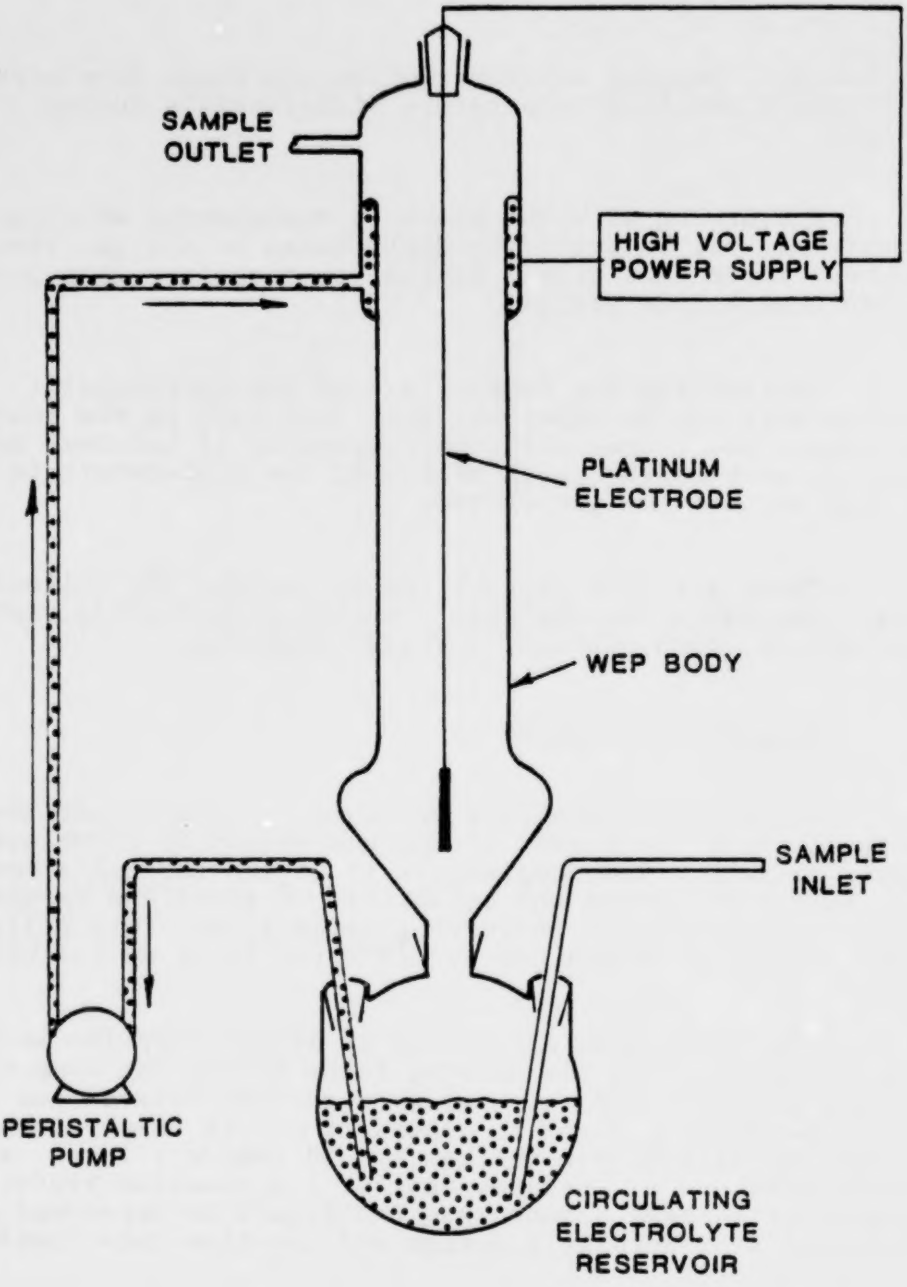

SAMPLE OUTLET
HIGH VOLTAGE POWER SUPPLY
PLATINUM ELECTRODE
WEP BODY
SAMPLE INLET
PERISTALTIC PUMP
CIRCULATING ELECTROLYTE RESERVOIR

Figure A-9. WET ELECTROSTATIC PRECIPITATOR apply, however, because maldistribution can occur from stream non-uniformity and from temperature differentials during collection.

Traversing with the probe is recommended when gaseous components may not be uniformly distributed in the gas stream. It has been shown that either laminar or turbulent flow conditions can create this problem.

Controlling the temperature of the particulate-collection unit may be important when this unit is the source of the sample gas. Some vaporous components of interest may condense or sorb on the particulates if the temperature is lower than that of the gas stream.

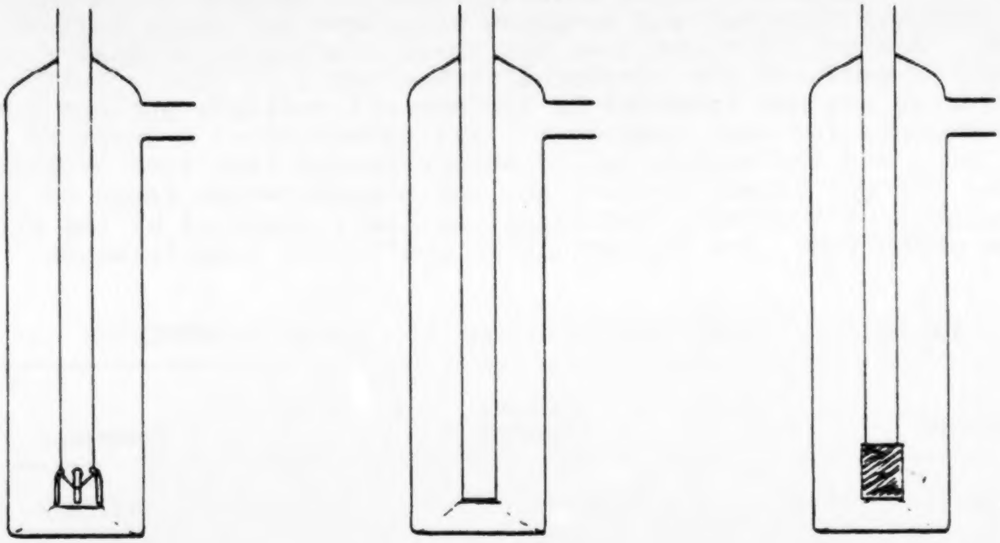
There are four general techniques for the collection of vapor components for analysis: sorption in liquids, sorption on solids, condensation, and grab sampling.

Sorption in Liquids -

Impingers or bubblers are used to collect and concentrate vapor-phase components of the gas stream by dissolution, reaction, or both. The sampled gas is passed through a specific reagent solution. Since the solubility of gases and vapors generally increases with decreasing temperature, this collection solution should be maintained at 273°K (32°F) in an ice bath.

The collection efficiency of liquid sorption techniques is dependent on the driving force making the component enter into solution and the degree of contact between gas and liquid. The driving force is dependent on the temperature, the mass-transfer rate across the gas-liquid boundary layer, and the vapor pressure of the component or its reaction products. The degree of contact between gas and liquid is dependent on the impinger's or bubbler's design and gas flow rate (residence time in solution).

Commonly used liquid impinger devices are illustrated in Figure A-10. These are sized to accommodate various ranges of solution volume and gas flow rate. Good practice dictates that a minimum of two impingers be used in series to allow the



SMITH-GREENBURG

MODIFIED SMITH-GREENBURG

FRITTED BUBBLER

Figure A-10. VAPOR COLLECTION DEVICES

collection efficiency to be calculated from separate analyses of the solutions.

Table A-2 lists several vapor or gaseous components of probable interest and sorption solutions for their collection. Analytical techniques for these components or their reaction products are presented in Section 5.0. The solutions presented are not intended to include all possible options but one example for each component. The selection of a sorption solution and the analytical technique should take into consideration the gas stream compositon, the concentration range of the component of interest, the detection limit required by the program objectives, and the potential analytical interferences.

Table A-2. SORPTION SOLUTIONS FOR VAPOR COMPONENTS*

Component	Sorption Solution	Reference
NH_3	5% H_2SO_4	Ref. A-3
HCN	10% NaOH	Ref. A-4
H_2S	2% $Zn(C_2H_3O_2)_2$	Ref. A-5
COS	7.5% $CaCl_2$/1% NH_4OH	Ref. A-4
CS_2	Alcoholic KOH	Ref. A-4
SO_2	6% H_2O_2	Ref. A-6
SO_3	80% Isopropanol	Ref. A-7
NO_x	5% H_2SO_4/H_2O_2	Ref. A-8
Trace Elements	0.2M $(NH_4)_2 S_2O_8$/ 0.02M $AgNO_3$	

* Grab sample drawn into evacuated glass vessel containing sorption solution.

Sorption on Solids -

Collection of components by sorption on solids, followed by their recovery through thermal desorption or solvent extraction is a rapidly developing area of sampling techniques.

These techniques provide for the simultaneous collection and concentration of components, analogous to the liquid sorption techniques discussed above. The collection and determination of organic components using solid substrates - particularly porous polymer resins (as used in gas chromatography), activated charcoal, silica gel, XAD-2 and Tennax - is the primary application of solid sorption techniques. Most applications are presently in the earily stages of development. Therefore, a definitive characterization of their use for the wide range of organic components of interest is needed. Before using a solid sorbent for a particular organic compound, the following factors must be considered and quantified:

- collection efficiency as a function of flow rate and temperature,
- breakthrough capacity,
- component stability, and
- recovery efficiency.

These factors must be determined empirically for each component, or combination of components, before a solid sorption technique can be considered reliable for quantitative determinations. Collection efficiencies can often be enhanced by collection at low temperature. If complete characterization of a technique is not feasible, the use of two or more collection devices in series can give an indication of collection efficiency and breakthrough capacity. Component stability can be enhanced by sample storage at low temperatures under an inert gas. Results not generated under these circumstances must be handled with considerable skepticism and can be considered semiquantitative at best.

Solid sorption techniques have received limited application for inorganic gaseous components. Silica gel has been used as a support for direct reading colorimetric tubes (Ref. A-9). These devices have been developed for a variety of components and are useful for semiquantitative surveys. Silica gel has long been accepted as a standard approach to the determination of moisture content of gas streams (Ref. A-10). The determination of mercury vapor by collection through amalgamation of gold or silver, followed by thermal desorption, has been extensively documented (A-11).

Condensation -

The viability of condensation, including cryogenic techniques, for a particular component in a gas stream can be roughly evaluated by comparison of the component's vapor pressure (at the condensation temperature) with its partial pressure (directly related to the concentration on a volume/volume basis) in the gas stream. The vapor pressure must be at least an order of magnitude below the partial pressure in the gas stream for a condensation technique to have any potential for application. In general, condensation techniques are more useful for organic components than for inorganic ones, because most inorganic gases require extremely low temperatures. Condensation or freezing at cryogenic temperatures (usually with liquid nitrogen) is very cumbersome and requires that the sample be analyzed immediately or stored at the collection temperature to avoid losses. Condensation and freezing of gas-stream moisture can cause severe plugging and dilution problems when cryogenic techniques are used. Determination of moisture content by a combination of condensation and silica-gel sorption is a widely practiced technique (Ref. A-10). This is an example of an often used combination of condensation backed up by solid sorption.

Condensation is often used as a clean-up procedure for removing condensables from a sample gas stream to minimize interferences when determining a noncondensable component. This is particularly useful for gas streams containing high levels of condensable organics. Although this approach is often useful, extreme caution must be exercised to avoid loss of the component by sorption in the condensed materials. Here, analysis of the condensate for the component of interest may be used as a check or correction procedure.

Grab Sampling -

The use of rigid or nonrigid containers for the collection of gas samples in the gas phase is termed grab sampling. There are two major sources of error which restrict the use of this technique: adsorption on (or reduction by) the container walls, and reaction of gas components with each other.

These effects can be minimized through the use of inert materials such as glass or teflon in container construction and in the preconditioning of the container prior to sampling. Analysis of grab samples should be conducted as soon after collection as possible, and sample stability as a function of time should be determined. The most difficult source of error to avoid is the loss of components by sorption in condensate (usually water vapor) produced during cooling of the sample. Maintaining the container at a temperature high enough to prevent condensation is not usually practical, and reheating rarely is effective. Removal of moisture by sorption on silica gel or by a permeation dryer prior to the container may be a solution if the component of interest is not sorbed on the desiccant or passed through the permeation dryer tubes.

As this discussion indicates, severe problems may arise with the reliability of grab sampling techniques and they can only be used with confidence for nonreactive fixed gases or following extensive verification. The sorption technique for NO_x listed in Table A-2 illustrates a modification of grab sampling to include a sorption solution in the collection vessel.

A-1.1.4 Metering Unit

With the exception of grab sampling (which often requires a vessel of known volume), all of the techniques described for particulate and vapor collection require measuring the sampled gas volume before calculating concentration in the gas stream from the analytical results. In addition, the sample-gas flow rate must be known in order to maintain isokinetic sampling rates.

The most commonly employed metering technique to provide a cummulative volumetric measurement is a dry gas meter, the type used for household natural-gas metering. These meters are available in a wide range of maximum flow-rate capacities and are useful down to a minimum flow rate of 0.1 cfm. Dry gas meters must be calibrated frequently against a standardized meter or a wet-test meter and then handled carefully to avoid inverting or jolting. The sample gas must be conditioned prior to metering by the drying and removing of corrosive components. To convert the meter readings to standard conditions, the inlet and exit meter temperatures and meter pressures must be recorded during sample collection. The use of wet-test meters in field situations is not recommended.

An alternative approach is to measure flow rate and total sampling time to provide the total gas volume. Rotameters and orifice meters are well suited for this function. A comprehensive discussion of these meters is available in Perry's Chemical Engineers' Handbook; equations are available for correcting rotameters and orifice meters for variations in gas temperature, pressure, density, and viscosity (Ref. A-12).

A-1.2 Continuous Monitoring

The results of an extensive sampling and analytical program may call for the continuous monitoring of some species in a gas stream. The basis for deciding which stream and analytical parameter to monitor must be a part of the overall test plan. The decision could be based on many factors, including the following:

- compliance with governmental regulations,
- reduction of undesirable chemical effects (including toxicity),
- process control, and
- research and development investigation.

Due to the repetitious and long-term nature of continuous monitoring, automated or instrumented systems are inherently more suitable than the manual techniques previously described. Physical conditions - including temperature, pressure, flow rate, and density - are conveniently monitored using commercially available instrumentation, such as normally is installed for process control. While not directly a part of the test plan, such instruments supply process information related to the testing.

The analytical parameters frequently of interest for continuous monitoring are discussed in the remainder of this section. While not intended to be all-inclusive, this discussion is a guide providing examples of continuous monitoring applications.

Continuous monitoring equipment should be selected only after all costs for initial purchase, installation, and maintenance are considered. An inexpensive instrument with frequent repair and calibration problems can be more expensive and less reliable than manual methods. The consequences of instrument failure for process operation and for the successful execution of the test plan are important considerations.

Planning for automated monitoring should take into account three areas of choice: sampling approaches, analytical determinations, and instrument calibration methods.

A-1.2.1 Sampling Approaches

There are two basic approaches for instrumentally monitoring a gas stream: extracting the sample from the stream for analysis and analyzing the stream in situ.

Extraction Systems -

The extractive approach is the oldest one with more information available on applications. After a probe is installed in the gas stream, the gas is drawn through the probe and then through a sample conditioning system. This system removes particulates and adjusts the sample to the appropriate temperature, pressure, and moisture content. The sample then enters the analyzer. Detailed attention to the sample conditioning system is required for maintaining sample integrity.

There are many advantages to extractive systems. They frequently are available at a lower cost and are more flexible in their application and location, because the analyzers are no longer subject to the temperature, pressure, and contamination problems associated with in-situ analysis. These problems are eliminated by the conditioning unit in an extraction system. Such a unit protects the analytical instruments by removing impurities from the stream and adjusting stream conditions to conditions for which the instrument has been calibrated. An extractive system can also be provided with a more representative sample by using a multiple-orifice probe or a multiple acquisition system. A combined sample-acquisition and conditioning system can supply a sample stream to several analyzers; also a single analyzer can handle samples from several streams.

One obvious problem with extractive systems is that if the species of interest is very reactive, the extractive and conditioning procedure can alter sample composition from actual stream composition. In such cases an in-situ system would be preferred.

In Situ Systems -

In situ continuous monitors of gas streams may in general be classified as optical or non-optical systems. In situ optical systems provide an average value of the light path over one diameter of the stack (possibly two diameters if the optical path is folded by a reflector). In situ analyzers have a limitation imposed by the physical parameters of the stream analyzed. They are, however, not subject to the limitations and possible loss of sample integrity present in a conditioning system. This makes them ideal for the more reactive species. The installation of an in situ system, however, is often more costly and requires more frequent maintenance. An in situ optical system requires, for example, periodic cleaning of the optical windows.

Some non-optical techniques are available for in situ monitoring. Also, some of the recently developed analyzers employ features of both in situ and extractive techniques. In one arrangement, the analyzer is contained in a porous housing extended into the gas stream. Because it is located in situ, the analyzed gas needs no conditioning to maintain stream conditions. Yet, by maintaining the analyzer slightly evacuated, the inflowing sample is filtered through the porous housing. Calibration is performed by pressurizing the porous container with known gas mixtures. Thus, the benefits of in situ conditioning and extractive filtration are combined.

A new in situ technique for optically analyzing stack gas just after it enters the atmosphere is based on laser optics that allow remote detection. While not at present commercially available, this technique shows great promise for ease of installation and flexibility in location.

A-1.2.2 Analytical Determinations

Sample analysis systems can use either the extractive or in situ techniques. These techniques can best be reviewed in terms of the analytical parameters to be monitored. In this text these parameters are considered under three categories: particulates, criteria pollutants in general, and other gaseous components.

Particulates -

The instrumental monitoring of particulates is normally limited to the determination of particulate loading (including particulate size distribution) - the concentration of mass within a given gas volume (as discussed in Section A-1.1.2). The guidelines for selecting manual sampling points and sample handling apply also to continuous monitoring. Particulate concentration is normally monitored by measuring collected particulate matter from a known volume of gas.

Devices for directly determining particulate concentration, including particulate concentration as a function of particle size, are currently marketed. These usually operate in a cyclic or batch mode and are complicated and costly. To maintain an isokinetic sampling rate, the flow rate must be automatically controlled, based on the output of a velocity-measuring device.

A more commonly used approach is the indirect determination of particulate concentration with an optical method. The optical density of the gas stream is monitored by passing the gas stream through a light beam. The relative particulate concentration is indicated by changes in optical density. The relationship between this optical density and particulate concentration is determined empirically, with the absolute particulate concentration estimated from the established relationship.

The particulate size distribution can be monitored by measuring the degree of light scattering caused by particulates in the gas stream. Unlike particulate concentration measurement, particulate size distribution is normally monitored by using an extractive technique outside the confines of the gas stream duct. Also, a large amount of clean, particulate-free air is normally required for sample dilution. These factors require extra attention to details of the sample acquisition and handling systems.

Criteria Pollutants -

Effluents from a coal gasification plant, especially the combustion products, will be monitored for "criteria pollutants" to meet requirements of government regulations. Besides particulates, these pollutants include two frequently monitored gases - sulfur oxides and nitrogen oxides. If the monitoring of these emissions is a direct result of government regulation, care should be taken to ensure that the installed systems are acceptable to the regulatory agency, in addition to providing the data required for the test program. The EPA has promulgated specifications and standards for instrumentation in over two dozen industries or processing areas (Ref. A-13).

Both in situ and extractive techniques are available to monitor these criteria species. Currently accepted instrumentation employs optical, wet chemical, electrochemical, or chemiluminescent methods for oxides of sulfur and nitrogen; the flame method is available for detecting oxides of sulfur. The remote (laser) in situ method mentioned earlier looks most promising for the measurement of SO_x and NO_x.

Other Gaseous Components -

Going beyond these criteria pollutants are the major gas and vapor components of the process and effluent gas streams. Important ones are illustrated in Table A-3. In this table, many gases are included in more than one category. There are continuous analytical methods for analyzing these species.

Table A-3. GAS AND VAPOR COMPONENTS

Fixed Gases	Acid Gases	Sulfur Species	Non-Condensable Hydrocarbons	Condensables
H_2	H_2S	COS	CH_4	H_2O
CO	CO_2	SO_x	C_2H_5	SO_3
N_2	SO_x	CS_2	C_2H_6	>C_6 Hydrocarbons
O_2	NO_x	H_2S	C_3 to C_6	
Ar	HF	RSH		
NH_3	HCl	RSR		
CH_4	HCN			

Although continuous-reading instruments are marketed for measuring moisture content, molecular weight, gas density, and total heat content, this discussion focuses on the two major approaches for the quantitative determination of such species: chromatographic and optical.

Process gas chromatography (GC) is an extractive technique and is probably the most widely applicable method. All of the gases listed can be analyzed with a process GC. In most cases, multiple analyses can be performed.

A typical process GC installation consists of a sample acquisition and conditioning system, a column for species separation and a detector. Each of these three components must be tailored to the particular task performed. In some cases, multiple columns and detectors can be used for one collecting instrument. The sample handling and conditioning considerations discussed earlier apply to GC analysis. Separation columns for process GC are available in many types. While a discussion of these is beyond the scope of this effort, detailed information is available from GC instrument manufacturers.

The GC detectors most often used in process instrumentation include three types: thermal conductivity (TC), flame ionization (FID) and flame photometric (FPD).

The TC detector will analyze all the species and is most commonly used. Its major drawback is its lack of sensitivity. Also, it cannot analyze high concentrations (several percent) of one species and low concentrations (< 100 ppm) of other species in the same sample. As a result, the TC is usually used for the analysis of "major" species in a gas stream.

The FID has a very large sensitivity range, almost four orders of magnitude. Flame ionization is also selective for hydrocarbons, so is widely applied to the analysis of organic species. Other advantages expand the usefulness of the FID. A sample may be introduced to the detector without prior separation and still obtain a total hydrocarbon value. Other techniques, such as the separation and catalytic hydrogenation of CO to form methane, extend the applications.

The FPD is selective for sulfur-containing species and is a very sensitive detector. These two characteristics make flame photometry very useful in the analyses of sulfur species, although the separation techniques for these species are often difficult. The major limitation of the FPD is its relatively narrow range of linearity (usually less than two orders of magnitude) with respect to concentration.

The other main continuous approach, optical analysis, is used in numerous commercially available instruments. The ability of many species to absorb a specific wavelength of light is the principle utilized. These analyzers detect light from the ultraviolet, visible, and infrared regions, employing either in situ or extractive techniques.

In nondispersive infrared (NDIR) analysis, the extrative mode is more common. This technique can be used for most of the species listed in Table A-3 (except for those having diatomic molecular structure), if interfering species can be masked. NDIR instruments are also unique in being convertible at minimal cost for monitoring an entirely different species - thus increasing their flexibility.

A-1.2.3 Calibration Methods

Quality control for instrumental monitoring is primarily a matter of frequent and careful calibration. These requirements are often specified in detail by the manufacturer, and sometimes by a governmental regulatory agency.

The basic approach is to check the analyses against known samples. Precision is ensured by the consistency of replication when a particular sample is retested repeatedly. Accuracy is ensured by periodic comparison with a standard having a known content. In addition, the instrumental results may be checked at any time by comparing them against the results of manual sampling and analysis.

A-1.3 Fugitive Gas Emissions

Fugitive gas emissions are those which are expelled directly into the environment without passing through any transport device such as a pipe, duct, or stack. They may be generated in enclosed areas such as buildings and transmitted to the environment through structural openings and vents, or they may result from open area sources such as leaking equipment, open storage piles, and effluent disposal areas.

For environmental assessment testing, fugitive emissions are assigned to one of two categories: specific source emissions and site source emissions. Examples of specific sources are leaking valves, coal piles, and grinding mill building vent. Examples of site sources are the coal gasification unit and the plant as a whole.

A-1.3.1 Sampling Point Selection

The selection of sampling points for fugitive emissions are based on the source type and a good deal of subjective judgment on the part of the sampling team. Sources must first be identified and categorized according to type. They must be significant enough to warrant sampling within test guidelines. Specific sources may be sampled from downwind of the source to determine atmospheric distribution or they may be sampled directly by enclosing the source. Site sources are usually sampled from both upwind and downwind locations to determine area distributions of pollutants. Specific sampling point selection is highly site-specific and depends on source size and location and homogeneity of emissions. These factors will have to be determined by pre-test site surveys.

A-1.3.2 Sampling Techniques

The analytical parameters measured by fugitive emission sampling are similar to those discussed for manual gas sampling (Section A-1.1). Basically, the parameters of interest include gaseous compounds, particulates, trace organic species, and trace elements.

The basic types of sampling methods for collecting area and source fugitive emissions are listed below.

- Area Emissions
  - High volume sampling
  - SASS train sampling
  - Grab sampling
  - Continuous sampling
- Source Emissions
  - Source enclosure followed by a sample or collection or pretreatment train similar to those discussed in Section A-1.1

High Volume Sampling -

High volume sampling involves drawing large volumes of air through a filter to trap particulates. A split stream from the sampler is passed through an adsorbent canister or impingers to trap organic or inorganic species. Grab samples may also be taken from this stream. This technique is used for area sampling. Figure A-11 shows a typical high volume sampling assembly.

SASS Train Sampling -

SASS train sampling has been previously discussed and is much like high volume sampling. The major difference is that the SASS train will collect particulate matter fractions, organic species, and gaseous species (by impingers).

Grab Sampling -

Grab samples are taken of the fugitive emissions for gas component analysis. These are usually taken in three liter evacuated vessels and are obtained either directly from the atmosphere or from the high volume or SASS train sample streams. The gas compounds analyzed would include those not collected by solid sorbents or impingers.

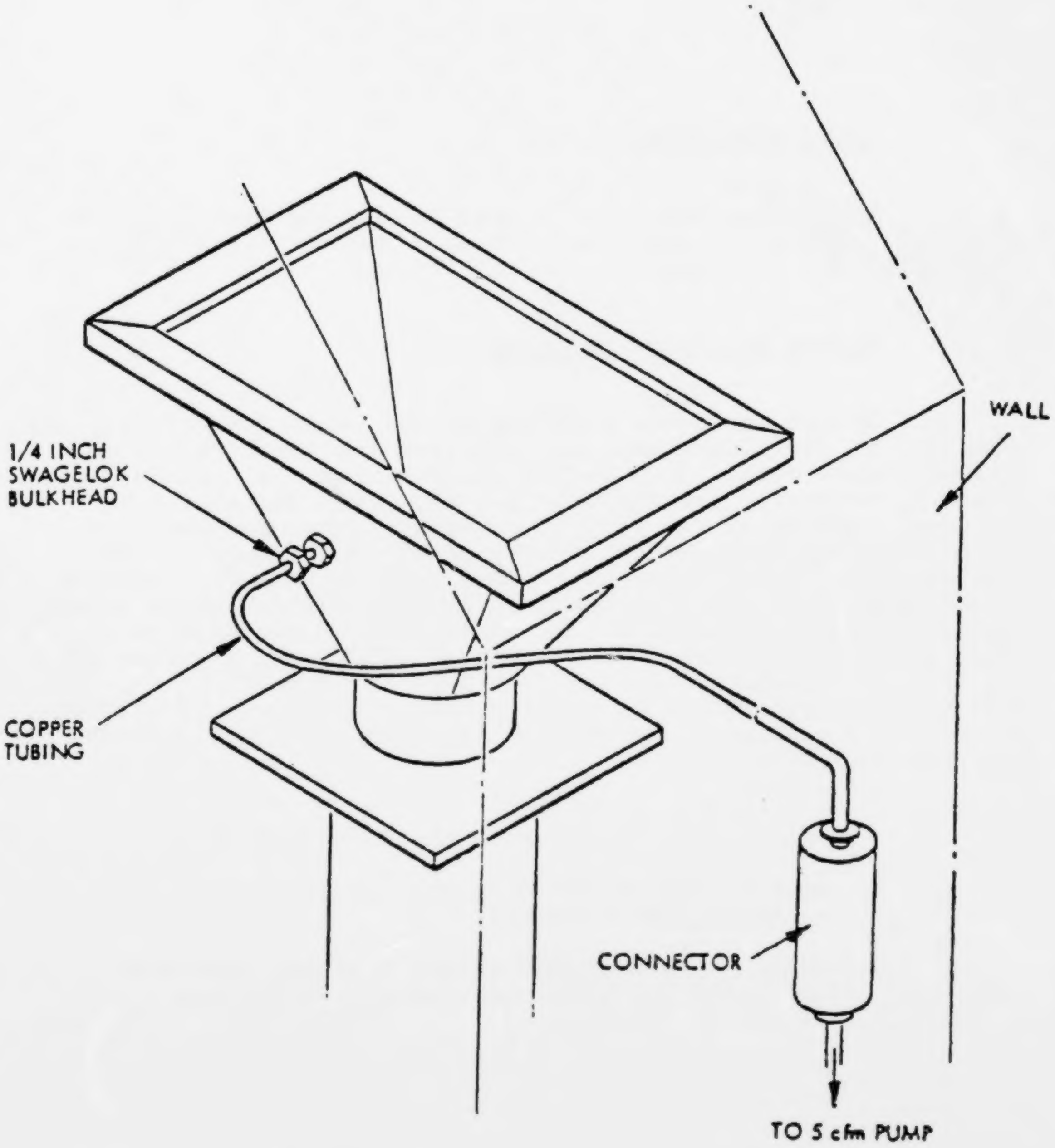

1/4 INCH
SWAGELOK
BULKHEAD
COPPER
TUBING
WALL
CONNECTOR
TO 5 cfm PUMP

Figure A-11. EXPANDED VIEW OF CONNECTIONS OF XAD-2 CARTRIDGE TO HIGH VOLUME SAMPLER

Continuous Sampling -

Continuous sampling is used to monitor area fugitive emissions. Currently continuous CO area monitors are being recommended for coal gasification facilities.

Source Enclosure Sampling -

Source enclosure sampling is the least defined sampling technique in the literature, but provides the most precise and representative data. This method involves bagging, tenting, or otherwise enclosing the emission source. Once the source is enclosed, samples of the trapped gases are taken and analyzed. If the rate of change in concentration of one or more of the species being leaked into the enclosure is monitored, a measure of the leak rate can be computed by knowing the enclosure volume during the sampling period. The source may be enclosed using a bagging or tenting technique. Mylar or teflon are a suggested bag material because it is easily shaped, relatively inert, and used for gas grab sample collection bags. Decisions on whether to enclose a source to measure its fugitive emissions depends upon the following:

- source size (can the source be enclosed),
- source temperature (bagging material may be temperature limited),
- expected composition of the fugitive emissions (will the gas component react with the bag material), and
- source location (can the source be accessed for enclosure).

Data which should be recorded by the sampling team during fugitive emissions sampling include:

- area data (temperature and air flow patterns),
- sampling location and method,

- emission source and characteristics (temperature), and
- sampling equipment operational data.

A-2 LIQUID SAMPLING

Liquid or slurry streams are numerous in a coal gasification facility, and the variety of materials composing them can be quite great. Fortunately, the methods for sampling them are relatively simple.

Multiphase liquid sampling poses special problems, as indicated by the following four general sample types:

- two liquid phases,
- high suspended solids content,
- pressurized liquid with dissolved gases, and
- high-temperature streams subject to phase change on sampling (condensable vapor, liquid that vaporizes with pressure reduction, and molten solid).

For a two-phase liquid, separation and separate analysis of two immiscible phases will probably be the simplest method of handling. The relative amounts of each phase are then used to calculate total material flows.

With liquid-solid slurry streams, the major problem is stream homogeneity. Unlike gases, which mix fairly easily, liquid streams tend to stratify because of their different viscosities and densities. Only extreme care can ensure that representative samples are obtained.

For pressurized single or multiphase liquid streams which contain dissolved gases it must be resolved whether the escaping gas needs analysis. Two sampling techniques may be used. In one method, the sample is taken at atmospheric pressure and the dissolved gases are allowed to escape; only the liquid portion of the sample is then analyzed. In the other, the sample is caught under process pressure in a suitable sampling bomb. Later the pressure is reduced, and the gases emitted are analyzed separately.

High-temperature streams may require the application of cooling methods to reduce the sample temperature to a level that is both below its boiling point and compatible with the sampling techniques used. Molten solid streams must be sampled by methods and equipment which allow for the fact that the sample will solidify on cooling.

A-2.1 Sample Point Selection

The preferred sampling points for liquid streams are existing valves, either in-line or on a side stream. These valves provide a ready source from the stream and should be used when compatible with the objectives of the test program. Other points of easy access are outflow orifices where the liquid streams flow into ponds, tanks, or other open surfaces. Open or noncontained streams may be sampled at any point compatible with accuracy requirements.

The major restriction in selecting sampling points is stream homogeneity. To ensure a well-mixed sample, sampling should be done just downstream from points of turbulence, such as elbows or pump-discharge lines. It may be necessary to have sampling valves installed at points where none exist.

A-2.2 Grab Sampling Methods

The selection of sampling method, the size of the sample, the frequency of collection, and the method of preservation must be based on the goals of the test program.

In selecting sampling methods for liquids the analytical techniques planned must also be considered. Analytical parameters for liquid slurry streams consist of four types:

- physical characteristics,
- inorganic species,
- organic species, and
- water quality parameters.

Table A-4 lists typical parameters for each of the first three categories. Overlap with water quality parameters is indicated in the table. The factors involved in deciding which parameters to analyze are defined by the test plan objectives. The sampling methods selected should be scrutinized for compatibility with the proposed analytical methods. In general, sample size will be determined by the number of analyses to be made and the specific requirements of each technique.

Samples may be taken at regular intervals over the duration of the test and then either analyzed individually or combined to give an averaged sample. If possible, the test duration should be long enough to cover normal process variations. For some cyclic processes, it may be best to sample at each step of the operation. In cases where sample requirements are less stringent, a single sample may suffice.

Grab sampling techniques may be adapted for liquid sampling according to test plan requirements. Depending on analytical requirements and stream characteristics in any given situation (as discussed below), either of two general methods may be appropriate: tap sampling and dipper sampling.

A-2.2.1 Tap Sampling

Tap sampling is used to collect liquid samples from enclosed pipes or storage tanks. Two tap systems are shown in Figure A-12. The simplest, shown in the bottom illustration, consists of a valve attached to the wall of the vessel or line from which the sample is drawn. To sample nonhomogeneous streams more accurately, the method shown in the top illustration of Figure A-12 is required. In this system, a probe is inserted

Table A-4. ANALYTICAL PARAMETERS FOR LIQUID AND SLURRY SAMPLES

Physical Characteristics

- pH *
- Solids Content (TDS and TSS)*
- Water Hardness*
- Specific Electrical Conductance*
- Acidity*
- Alkalinity*
- Turbidity*
- Temperature

Inorganic Species

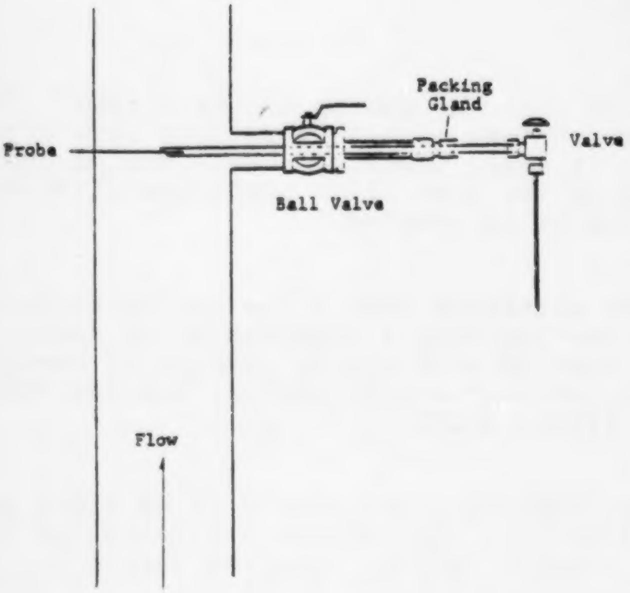
- Dissolved Oxygen*
- Ammonia
- Chloride
- Fluoride
- Sulfate
- Sulfite
- Sulfide
- Nitrate
- Nitrite
- Phosphate
- Cyanide
- Carbonate
- Iodide
- Orthophosphate
- Total Phosphate
- Major Elements:
  - S
  - Al
  - Ca
  - Fe
  - Na
  - Mg
  - P
  - K
  - Si
  - Ti
- Trace Elements:
  - Sb
  - As
  - Be
  - B
  - Cl
  - Cd
  - Cr
  - Cu
  - F
  - Pb
  - Li
  - Mn
  - Hg
  - Mo
  - Ni
  - Se
  - Tl
  - U
  - V
  - Zn

Organic Species

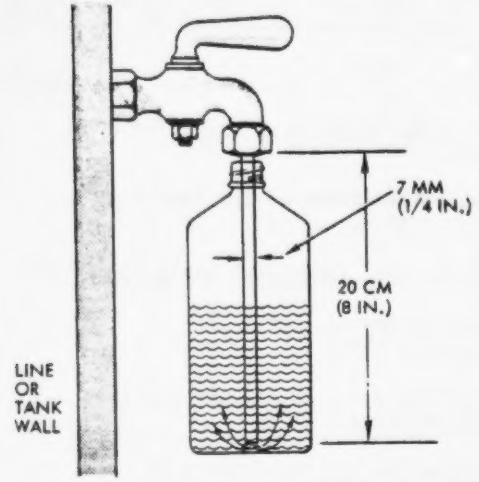
- Biological Oxygen Demand (BOD)*
- Chemical Oxygen Demand (COD)*
- Oil and Grease*
- Phenol
- Total Organic Carbon
- Speciation;
  - Polynuclear Aromatics
  - Heterocyclics
  - Halogenated Organics
  - Aromatics
  - Other Hydrocarbons

---

* Water-quality parameters


Packing Gland
Probe
Valve
Ball Valve
Flow

Sampling Configuration using Probe through Existing Valve for Liquid Streams


7 MM (1/4 IN.)
20 CM (8 IN.)
LINE OR TANK WALL

Assembly for Tap Sampling *

Figure A-12. TAP SAMPLING TECHNIQUES

* Reprinted by permission of the American Society for Testing and Materials, copyright 1973.

through a valve into the center of the stream. This method minimizes the problems caused by reduced flow along the walls of the pipe. It does, however, create design problems, since the seals and valves must allow probe insertion without leaks from the stream being sampled.

Some alternate sample tap configurations may be used for accurate testing when a representative sample can more easily be obtained, such as with static samples of homogeneous liquids. These provide representative samples, but are more difficult to install (see Figure A-13).

Tap sampling lines should be as short as possible to facilitate flushing. The samples are collected by inserting the sample line, usually Teflon, into the sample bottle so that it extends nearly to the bottom to minimize air entrainment in the sample. The sample line and bottle should be flushed thoroughly with sample material before a portion is retained. Specific examples of tap sampling can be found in the references cited in Table A-5.

Table A-5. LIQUID SAMPLING METHOD REFERENCES

Manual	Reference No.
1973 Annual Book of ASTM Standards, Pt. 23, "Water; Atmospheric Analysis."	Ref. A-14
ASTM, "Standard Recommended Practice for Sampling Industrial Chemicals, " 1973.	Ref. A-15
EPA, Handbook for Monitoring Industrial Wastewater, 1973	Ref. A-16
EPA, IERL-RTP Procedures Manual, Level 1: Environmental Assessment, 1976.	Ref. A-17
EPA, Tentative Procedures for Sampling and Analysis of Coal Gasification Processes, 1975.	Ref. A-18
ERDA, Assessment, Selection and Development of Procedures for Determining the Environmental Acceptability of Synthetic Fuel Plants Based on Coal, Revised Report, 4 vols.	Ref. A-19
Radian Corp., Sampling Plan, Characterization of the Effluents from the CO_2 Acceptor Process, 1976.	Ref. A-20

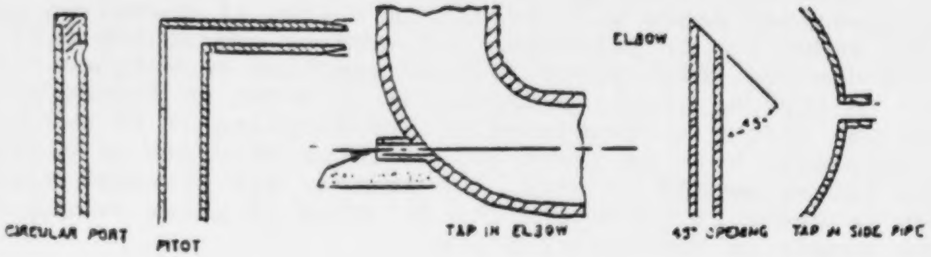

CIRCULAR PORT
PITOT
TAP IN ELBOW
ELBOW
45°
45° OPENING
TAP IN SIDE PIPE

Figure A-13. VARIOUS SAMPLE TAP INSTALLATIONS (Ref. A-15)*

---

* Reprinted by permission of the American Society for Testing and Materials, copyright 1973.

The temperature and pressure of the stream being sampled are not as critical in sampling liquid and slurry streams as they are with gas sampling. In general, high- and low-pressure liquid and slurry lines may be sampled by the standard tap techniques described. Care should be taken that valves on high-pressure lines are opened slowly to prevent injury to personnel. Sampling personnel should also be aware of the possibility of the sudden surge in the flow of sample systems due to the release of plugs in the probe or tap. Plant management should be consulted when any high-pressure lines are to be sampled, and plant safety regulations followed.

Open tap sampling of high-pressure liquid streams containing dissolved gases will result in a loss of dissolved gases after the reduction in pressure. If samples containing dissolved gases are desired, high-pressure bomb-sampling techniques must be used. A typical sampling apparatus is shown in Figure A-14. The bomb can either be evacuated before sampling or it may be filled initially with an inert gas, such as nitrogen or helium. When the latter method is used, the initial gas pressure must be known in order to calculate the dilution of gases released from the sample on depressurization.

The tap sampling of liquids flowing at subatmospheric pressure requires pump assistance to remove the sample. Figure A-15 shows the necessary equipment.

The tap sampling of liquid or slurry streams at high temperature (*i.e.*, above the liquid boiling point) requires special procedures. The liquid sample must be cooled to a temperature below its boiling point before its entry into the sample container or it will flash vaporize. The sample is cooled by passage through an air or water jacket system before collection (see Figure A-16). Again, care must be taken to thoroughly flush all parts of the system before material is retained for analysis.

In most cases, the use of a cooling system will cause some loss of sample integrity. A loss of material through deposition on the cooled wall is unavoidable. In some instances, plugging of the sample line will result. These problems can be minimized if the sample is cooled just enough to handle, but not below the temperature at which sample integrity is shown to be lost.

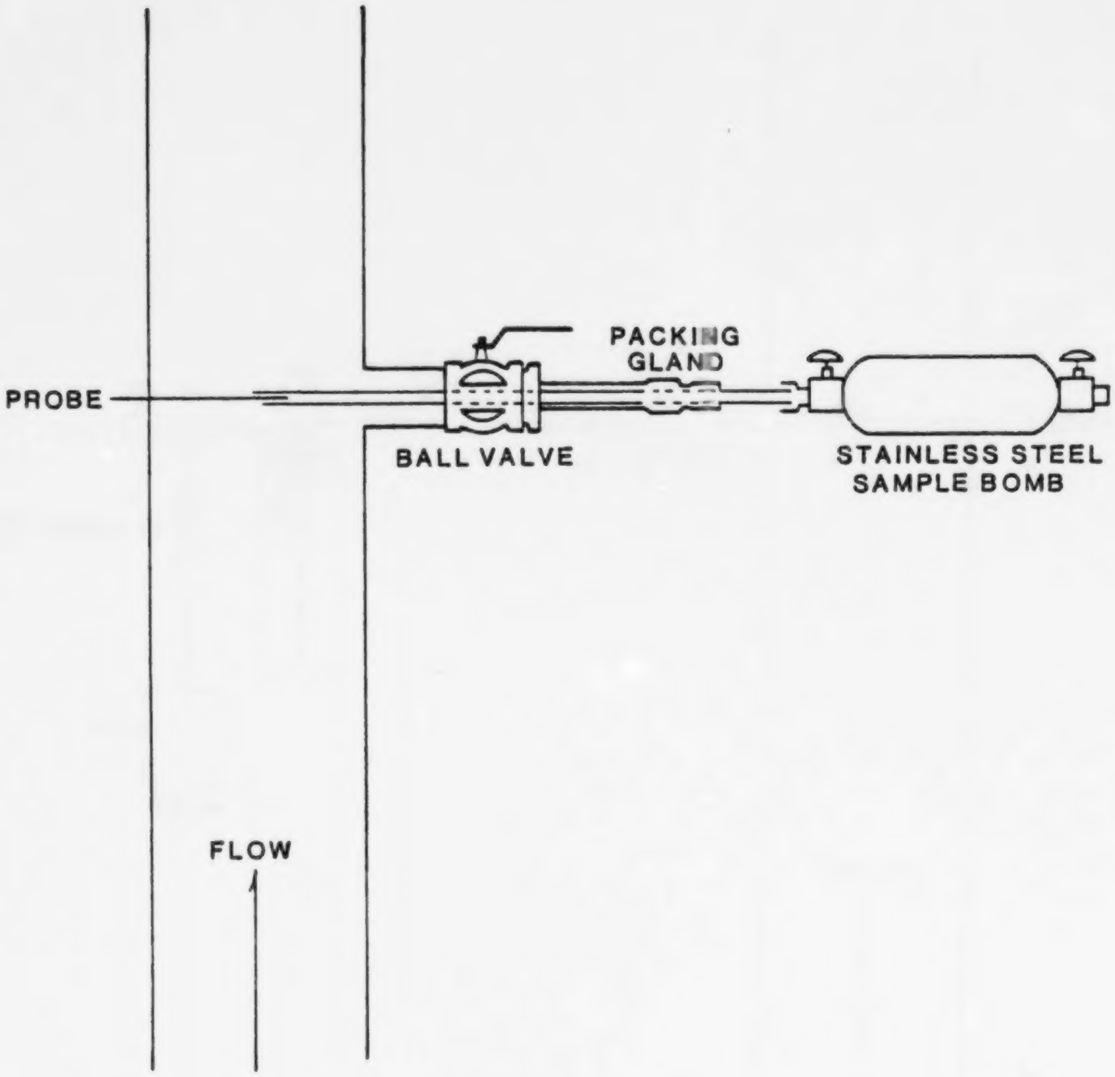

PACKING GLAND
PROBE
BALL VALVE
STAINLESS STEEL SAMPLE BOMB
FLOW

Figure A-14. TAP SAMPLING FOR HIGH PRESSURE STREAMS

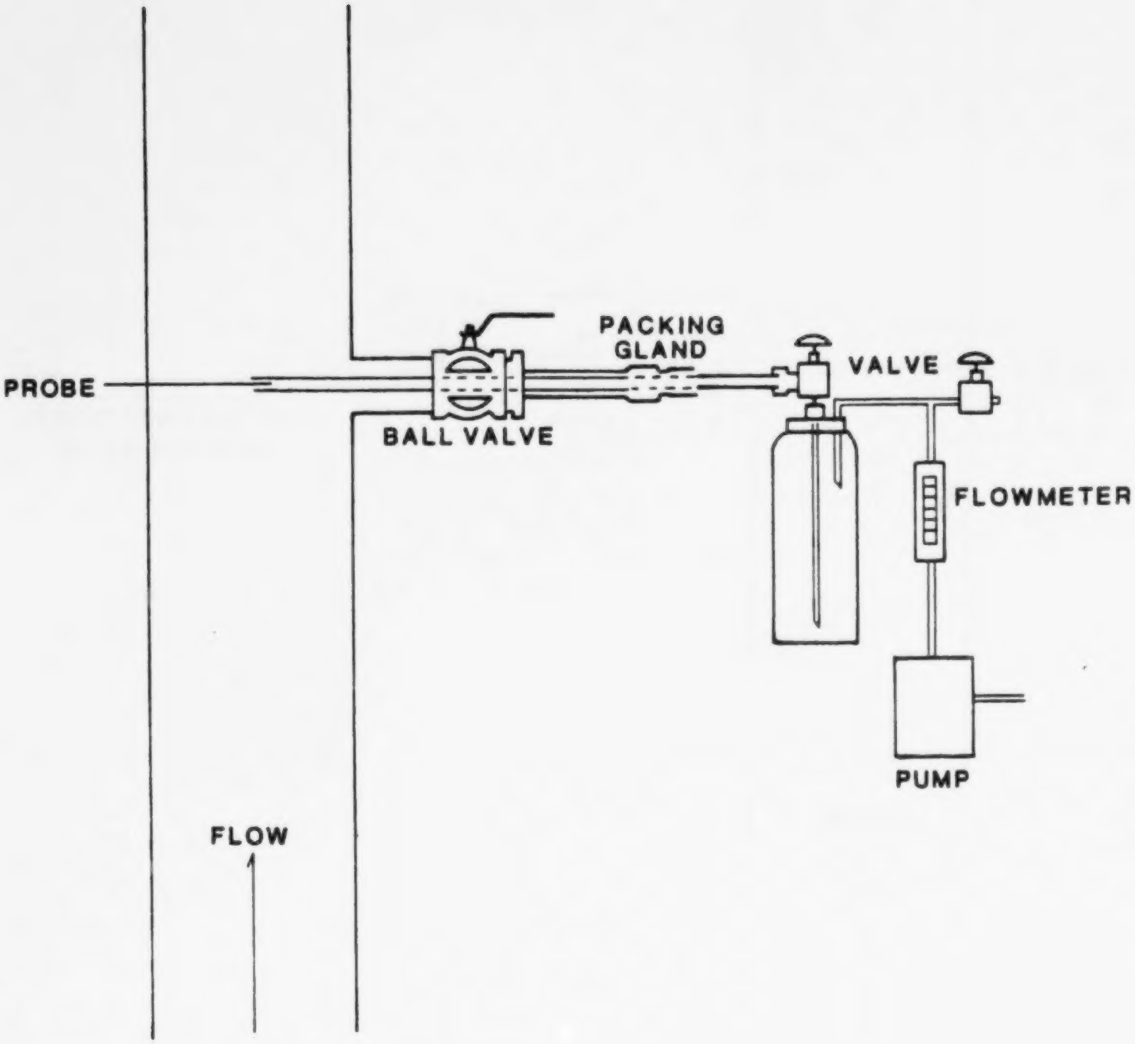
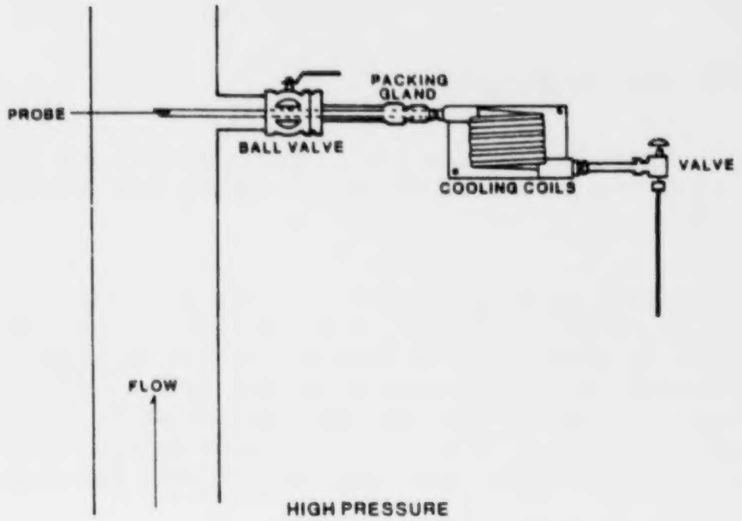
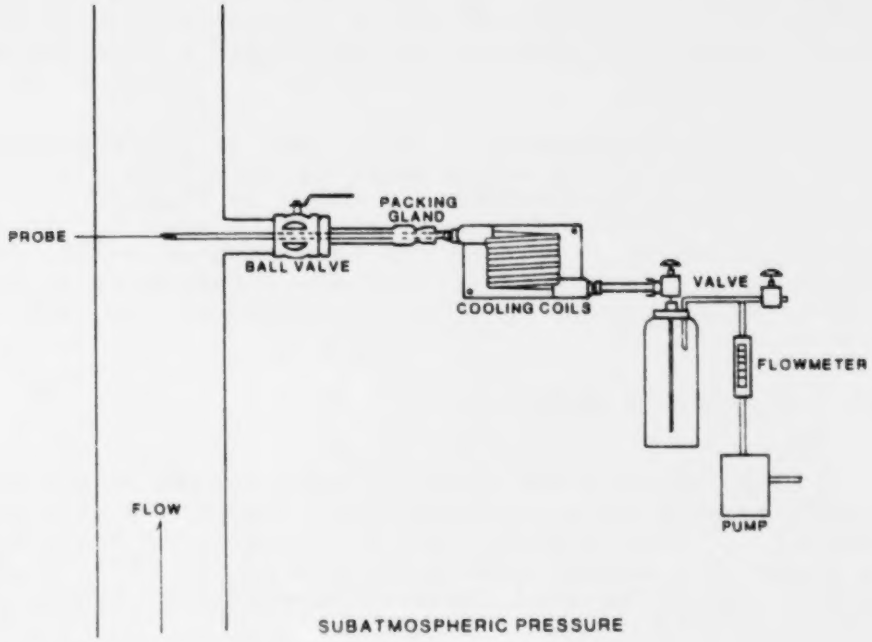

PACKING GLAND
VALVE
PROBE
BALL VALVE
FLOWMETER
PUMP
FLOW

Figure A-15. PUMP ASSISTED TAP SAMPLING OF SUBATMOSPHERIC LINES


PROBE
PACKING GLAND
BALL VALVE
COOLING COILS
VALVE
FLOW

HIGH PRESSURE


PROBE
PACKING GLAND
BALL VALVE
COOLING COILS
VALVE
FLOWMETER
PUMP
FLOW

SUBATMOSPHERIC PRESSURE

Figure A-16. SAMPLING METHODS FOR HIGH TEMPERATURE STREAMS

A-2.2.2 Dipper and Thief Sampling

Dipper sampling is for collection at liquid surfaces, whereas thief sampling collects material below the surface of a contained liquid.

The dipper sampling method is useful for sampling open ditches or sluices, storage tanks, and outflows from open pipe ends. The dipper is made with a flared, Teflon-coated bowl and a handle long enough to allow access to the areas being sampled. Multiple samples, if necessary, may be collected to obtain a sufficient sample volume. If possible, streams should be sampled at points where they are stagnant or not flowing.

A variation on the dipper method that provides a much more representative sample is collection where the stream flows out the end of a roughly horizontal pipe or flume. An inert container with sharp parallel sides is passed at an even rate through the falling stream, obtaining a full cross section of the stream (Figure A-17). The container should not be allowed to overflow if the effects of stream stratification or a representative proportion of solids in the liquid stream are desired.

If the sampling of a large tank or other stagnant vessel is unavoidable, a thief sampling procedure should be used. Thief sampling equipment is shown in Figures A-18 and A-19. A sample thief (or bailer) should be used to obtain samples from several depths in the tank (Figure A-20). Some thiefs are available which will collect a sample at an even rate while it is being pulled up from the bottom of the tank.

A-2.3 Continuous Sampling

Samples obtained from a liquid stream on a continuous basis will be much more representative than those obtained on a grab basis. If this higher level of accuracy is required, a sample probe of a design similar to one of the three shown in Figure A-21 should be used, unless the stream is known to be a homogeneous liquid.

The sample can be withdrawn and transferred to a container in different ways. The sample may be withdrawn periodically at a uniform rate. This can be done in increments with a smaller

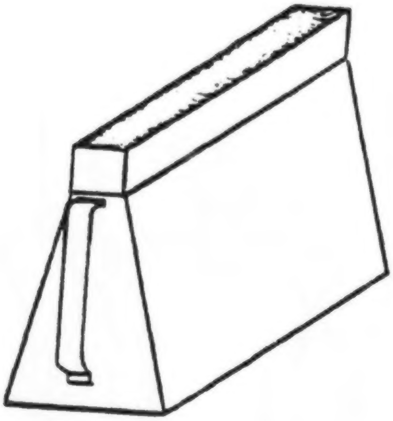


Figure A-17. STREAM SAMPLING CUP
(Ref. A-15)*

*Reprinted by permission of the American Society for Testing and Materials, copyright 1973.

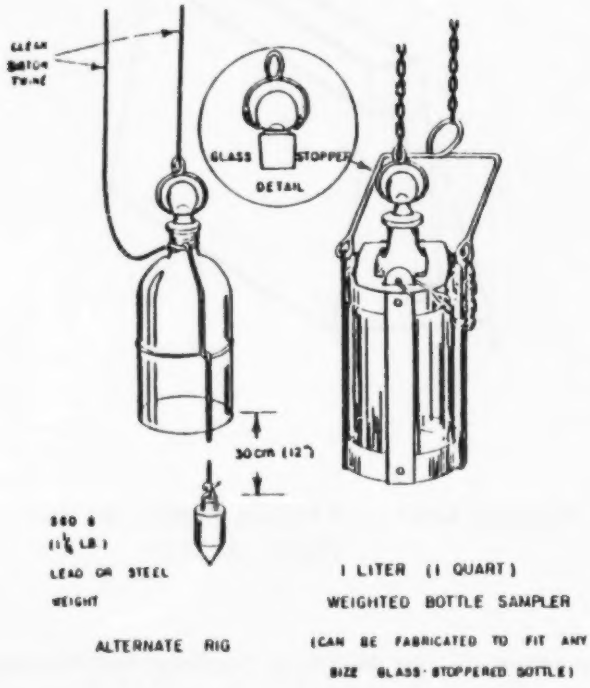
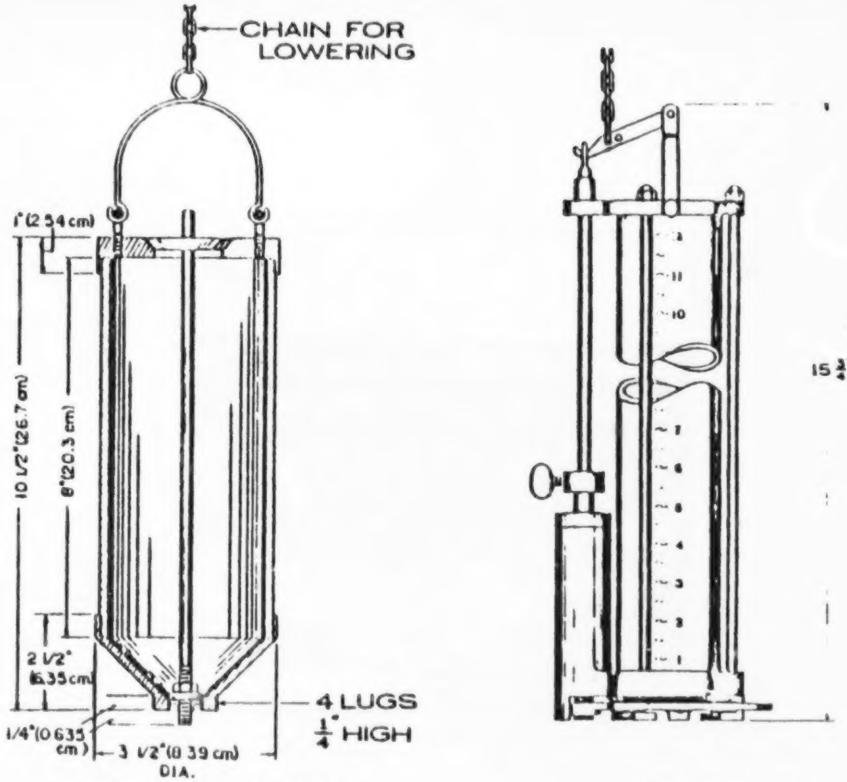

CLEAN COTTON TWINE
GLASS STOPPER
DETAIL
30 cm (12")
550 g
(1¼ LB.)
LEAD OR STEEL
WEIGHT
ALTERNATE RIG
1 LITER (1 QUART)
WEIGHTED BOTTLE SAMPLER
(CAN BE FABRICATED TO FIT ANY
SIZE GLASS-STOPPERED BOTTLE)

Figure A-18. ASSEMBLY FOR BOTTLE SAMPLING*

---

* Reprinted by permission of the American Society for Testing and Materials, copyright 1973.


CHAIN FOR LOWERING
1" (2.54 cm)
10 1/2" (26.7 cm)
8" (20.3 cm)
2 1/2" (6.35 cm)
1/4" (0.635 cm)
3 1/2" (8.39 cm) DIA.
4 LUGS 1/4" HIGH
12
11
10
7
6
5
4
3
2
1
15 3/4" (40.0 cm)

(a) Bomb-Types Sampling Thief

(b) Core Thief, Tap-Type

Figure A-19. SAMPLING THIEFS *

---

* Reprinted by permission of the American Society for Testing and Materials, copyright 1973.

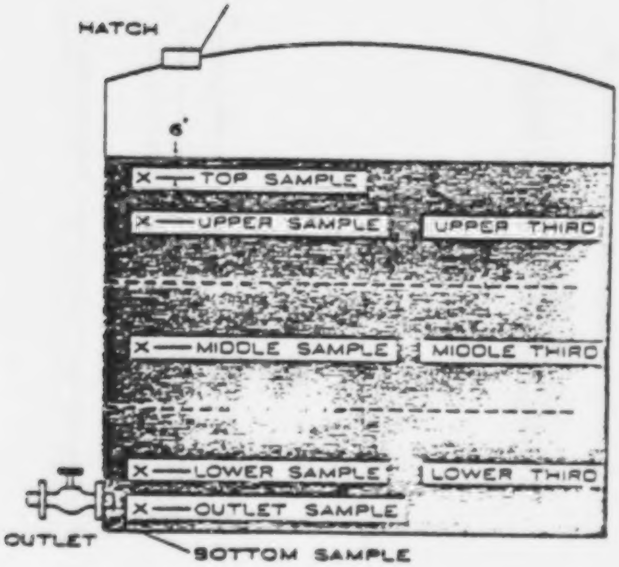

HATCH
6"
X — TOP SAMPLE
X — UPPER SAMPLE
UPPER THIRD
X — MIDDLE SAMPLE
MIDDLE THIRD
X — LOWER SAMPLE
LOWER THIRD
X — OUTLET SAMPLE
OUTLET
BOTTOM SAMPLE

Figure A-20. SAMPLING DEPTHS FOR THIEF SAMPLES (Ref. A-15)*

---

* Reprinted by permission of the American Society for Testing and Materials, copyright 1973.

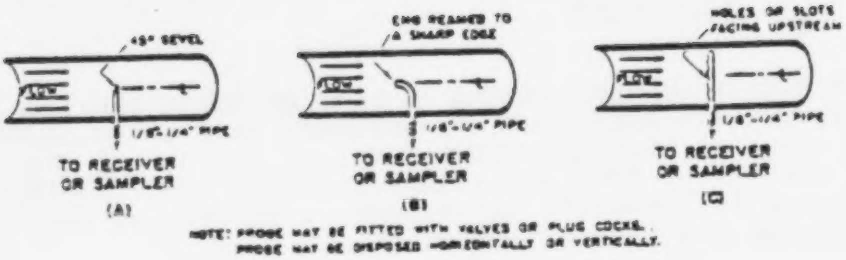

45° BEVEL
END REAMED TO
A SHARP EDGE
HOLES OR SLOTS
FACING UPSTREAM
FLOW
FLOW
FLOW
1/8"-1/4" PIPE
1/8"-1/4" PIPE
1/8"-1/4" PIPE
TO RECEIVER
OR SAMPLER
TO RECEIVER
OR SAMPLER
TO RECEIVER
OR SAMPLER
(A)
(B)
(C)
NOTE: PROBE MAY BE FITTED WITH VALVES OR PLUG COCKS.
PROBE MAY BE DISPOSED HORIZONTALLY OR VERTICALLY.

Figure A-21. SAMPLING PROBES
(Ref. A-15)*

* Reprinted by permission of the American Society for Testing and Materials, copyright 1973.

time interval between each unit volume fraction of the sample, thus providing a representative sample. The continuous sampling of a slurry in the most representative manner requires isokinetic sampling (discussed in Section A-1), with the velocity of the stream equaling the velocity at which the sample enters the sample probe. This assures that suspended solids are included in their proper proportion.

During continuous sampling, it is also possible to remove solids if desired by filtering or centrifuging, and to add the required preservatives as the sample is collected.

A-3. SOLID SAMPLING

Solids commonly found in coal gasification facilities are fuels, process additives, by-products, and waste products. They can range in size from fine power to lumps, and they can vary in consistency from dry solids to thick, non-flowing pastes. To accomodate all possible situations, a variety of sampling techniques are required.

The types of analyses performed on solids samples are highly dependent on the material sampled. For solid piles or streams, the nature of the analytical method rarely affects the sampling method used, although the handling and preservation methods are affected.

The sampling plan designer may need to arrange for solid samples from either of two general kinds of solids source: unit aggregations and process conveyors.

The unit aggregations are either large and stationary or they are transport containers. Solids used or produced in the gasification processes in large quantities are usually found stored in large open piles or enclosed silos. Both storage and transport units yield samples which may have already been composited, but with differing compositing periods. The stratification of solids in such static locations can make obtaining a representative sample difficult.

Samples from process conveyors represent solid materials being used continually during defined periods and under defined operating conditions. These streams, therefore, are the important ones for material balances and control-module response tests.

Sampling methods for solids use two general techniques, grab sampling and grab-and-composite sampling. Grab sampling is the general sampling technique used where low precision is required. Grab-and-composite sampling is the more precise technique. In most cases, the difference between the two is only a matter of degree; the sample collecting methods are identical. In the second, grab samples are collected periocally over the duration of the test, then composited to form a single sample. The following sections present more detailed sampling procedures for the various sources of solid samples. References for specific methods are cited in Table A-7. Although most of these methods are for coal, they are readily adaptable to other solid streams.

Table A-7. REFERENCES FOR SOLID SAMPLE COLLECTION AND HANDLING

Reference No.	Comments
Ref. A-21	General considerations for the collection of samples to measure trace components
Ref. A-22	ASTM Method D 2013-72: sample handling
Ref. A-22	ASTM Method D 2234-74: gross sample collection
Ref. A-15	ASTM Method E 300-73: sample handling and collection

A-3.1 Sampling Methods for Storage Facilities and Transport Containers

Solids encountered in coal gasification facilities are usually stored in piles or contained in enclosed bins with relatively large circumference and depth. The selection of sampling techniques for these materials will depend upon the test requirements, the sample pile form, and its accessibility. There are three basic methods: the shovel technique, the pipeborer technique, and the auger technique.

The shovel technique is used to remove a sample from the perimeter of a pile. Although this is the simplest solids sampling technique, it may well be inadequate. Unless there is reason to believe that the pile is homogenous, it may result in a highly nonrepresentative sample.

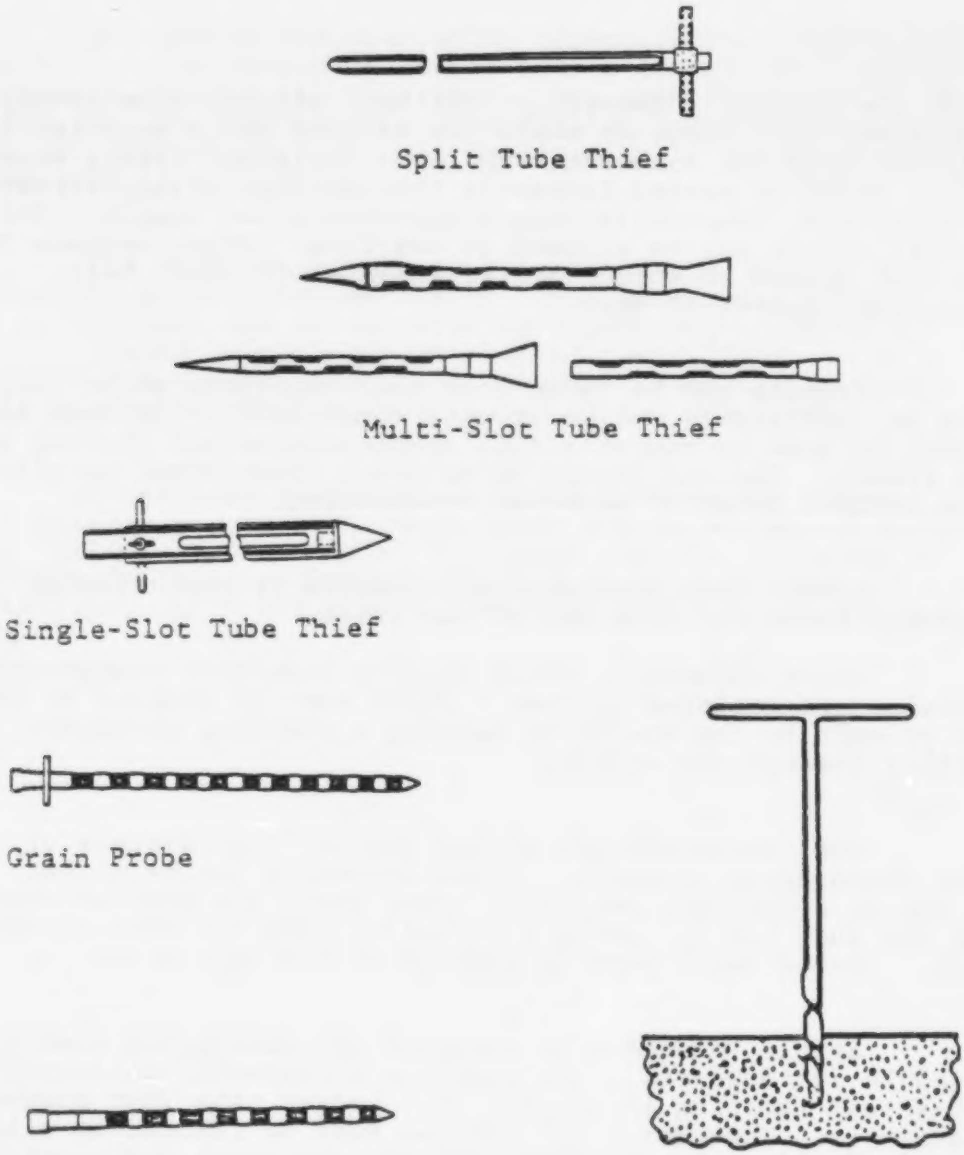
Somewhat more representative samples of materials stored in piles, silos, or bins can be obtained using boring techniques. These techniques involve inserting a pipe into the pile from top to bottom; the sample in the pipe represents a vertical composite of the pile. This technique cannot be used, however, with wet, coarse-grained, or lump materials. Small borers can be used to sample solids in sacks if the borers can reach to the bottom of the container.

There are two basic designs used for pipe borer sampling. The first is a straight length of pipe tapered at the insertion end. This is plunged through the pile, and the sample-filled pipe is withdrawn. The second type, a solids thief, is used when a more vertically representative sample is desired. It is made of two close-fitting concentric pipes, each with a sealed conical base and longitudinal slots in the walls (see Figure A-22). The thief is inserted with the slots non-aligned (turned away from each other). When it is in position, the pipes are rotated (relative to each other) so that the slots are aligned and provide access to the center of the inner pipe. The openings through which a sample flows (either the end of the simple borer or the thief slots) should be larger than the largest particle size to be included in the sample. Thief design variations are shown in Figure A-22.

The auger sampler is particularly suitable for sampling materials that are packed too tightly for pipe or thief techniques. An auger (Figure A-22) is like a large drill bit which is turned into the pile from the top. When the auger is withdrawn, the sample is packed in the helical grooves. If necessary to prevent sample spilling, it can be enclosed in a casing.

A-3.2 Sampling Methods for Process Conveyors

Process conveyors are the preferred sources for collecting representative samples of solid materials, because there is less segregation according to particle size, and the material obtained is often a sample of solids actually being



Split Tube Thief

Multi-Slot Tube Thief

Single-Slot Tube Thief

Grain Probe

Missouri Trier

Auger Sampler

Figure A-22. SOLIDS SAMPLING EQUIPMENT
(Ref. A-15)*

---

* Reprinted by permission of the American Society for Testing and Materials, copyright 1973.

used in the process. Generally, the best samples from conveyors are obtained at a terminus where the exiting solid material falls vertically from the conveyor. An inert container having sharp parallel sides is passed laterally through the falling stream at a uniform rate, thus collecting a representative sample. This container should not be allowed to overflow. Other methods for collection depend on which type of conveyor is used: belt, ladder-tray, screw, or duct.

Samples may be taken from belt conveyors while they are moving or, preferably, while stopped momentarily. In both cases, a shovel is used to remove a full cross-section cut (having parallel sides). The cut should be at least three times as wide as the largest piece of material encountered.

Ladder-tray conveyors are sampled by periodically removing a shovelful from one of the trays.

Screw conveyors, which usually transport sludge-type materials, are enclosed systems. These must be sampled at the inlet or exit to the system by passing a sampling container laterally through the stream.

Duct conveyors are either gravity-feed systems or employ chain-drive scrapers. These conveyors can be either open top or completely enclosed. Open ducts are sampled from above the duct top by taking a shovelful from the duct-conveyed solids. Closed ducts must be sampled at the exit point.

Sample reduction is required for making the sample manageable for analysis. The quantity of material collected in solid-stream sampling is usually much larger than that needed for analysis. Therefore, the samples must be reduced in size without affecting the distributions of components and particle sizes. Two methods are generally accepted for accomplishing this: the coning and quartering method and the riffling method.

It is frequently necessary to reduce the sample's particle size before this sample reduction can begin. Above a certain particle size, coning and quartering a sample into smaller quantities is not a valid technique. Particle size reduction is also necessary for most rifflers.

The coning and quartering technique is illustrated in Figure A-23. The sample is shaped into a conical pile which is then sharply divided into quarters. Two opposite portions are combined and the composite is then further reduced by again coning and quartering. This is repeated until a sample of the desired size is obtained.

The riffling technique is a mechanical way of subdividing the sample systematically. The mechanical devices known as rifflers are illustrated in Figure A-24. When the sample is poured evenly over the top of the riffler, it is divided into two equal fractions. Further sample size reduction is accomplished by recycling one of the fractions.

Continuous samplers for solid streams are commercially available. In most cases, they are an automated version of the falling-stream sampler described earlier, followed by an automated sample-reduction system such as a riffler (or a whistle pipe), with the excess sample returned to the solid stream.

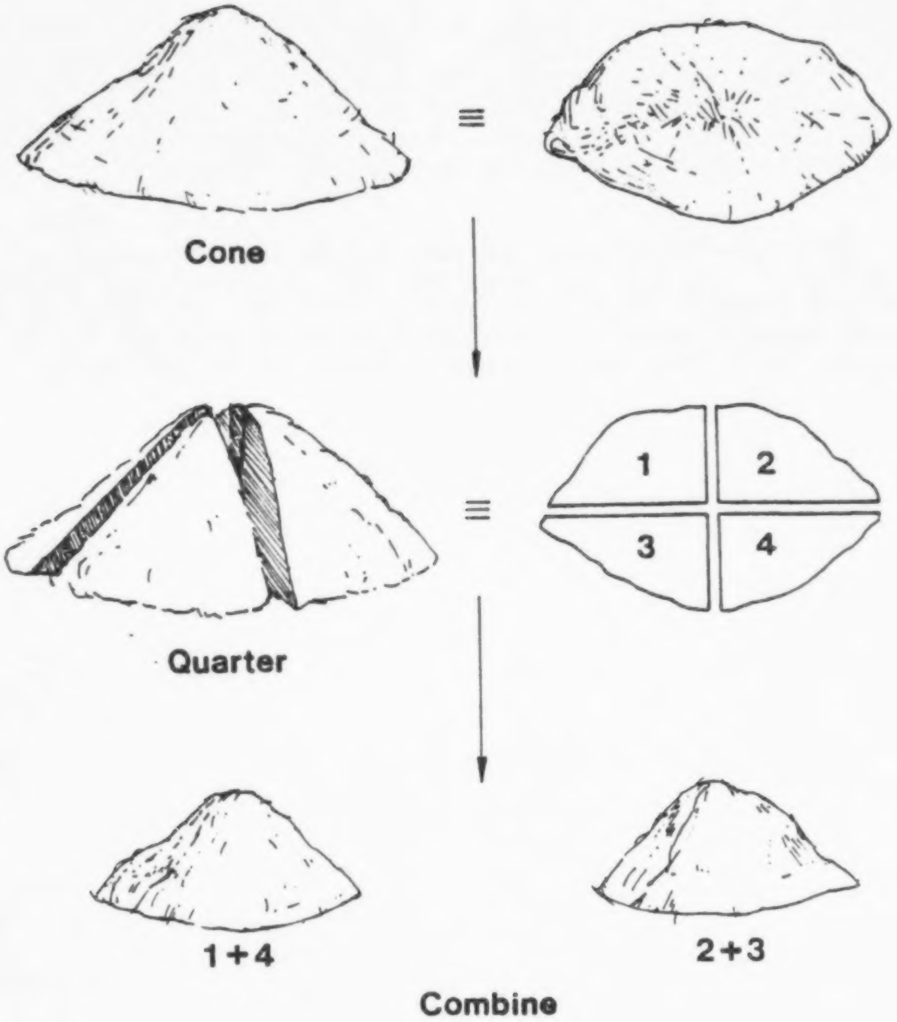
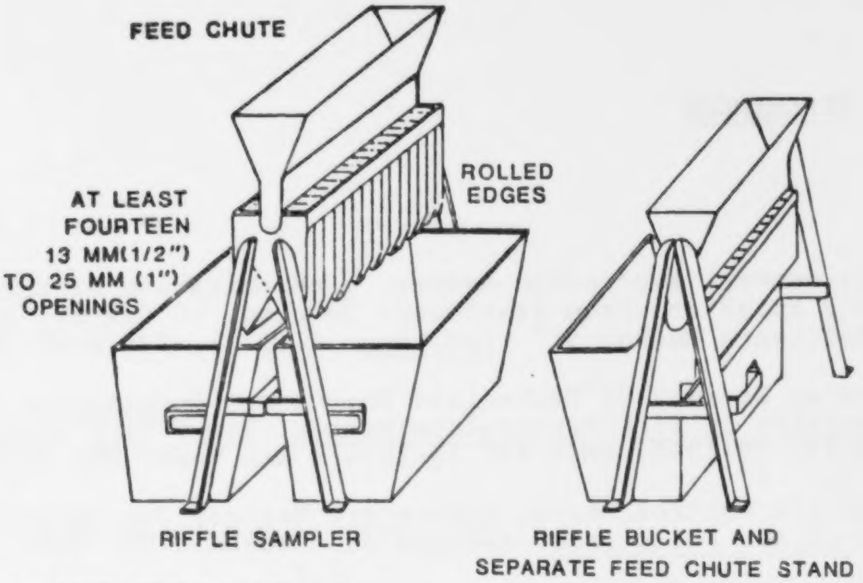
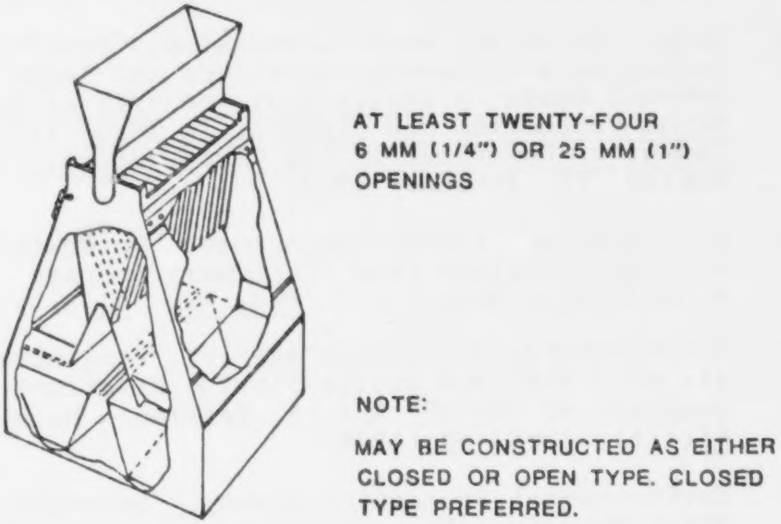

≡
Cone
≡
1
2
3
4
Quarter
1+4
2+3
Combine

Figure A-23. CONING AND QUARTERING


FEED CHUTE
AT LEAST FOURTEEN 13 MM(1/2") TO 25 MM (1") OPENINGS
ROLLED EDGES
RIFFLE SAMPLER
RIFFLE BUCKET AND SEPARATE FEED CHUTE STAND

A. LARGE RIFFLE SAMPLERS


AT LEAST TWENTY-FOUR 6 MM (1/4") OR 25 MM (1") OPENINGS
NOTE:
MAY BE CONSTRUCTED AS EITHER CLOSED OR OPEN TYPE. CLOSED TYPE PREFERRED.

B. SMALL RIFFLE SAMPLER

Figure A-24. RIFFLES FOR SAMPLE SUBDIVISION
(Ref. A-18)

A-4 REFERENCES

A-1. Environmental Protection Agency, "Determination of Particulate Emissions From Stationary Sources, 40 CFR 60, App. A, Reference Method 5," Fed. Reg. 41(111), 23076-83 (1976).

A-2. American Society of Mechanical Engineers, Determining the Properties of Fine Particulate Matter, Power Test Codes. ASME PTC 28-1965, ANSI PTC 28-1974. New York, NY, 1965.

A-3. Texas Air Control Board, Laboratory Methods for Determination of Air Pollutants, Revised ed. Austin, TX, June 1976.

A-4. Jacobs, Morris B., The Analytical Toxicology of Industrial Inorganic Poisons. New York, NY, Interscience, 1967.

A-5. Texas, State of, Water Commission, Groundwater and Electronic Data Processing Divisions and Texas Water Pollution Control Board, A Statistical Analysis of Data on Oil Field Brine Production and Disposal in Texas for 1961 From an Inventory Conducted by the Texas Railroad Commission. Austin, TX, February 1963.

A-6. Environmental Protection Agency, "Determination of Sulfur Dioxide Emissions From Stationary Sources, 40 CFR 60, App. A, Reference Method 6," Fed. Reg. 41(111), 23083-85 (1976).

A-7 Environmental Protection Agency, "Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources, 40 CFR 60, App. A, Reference Method 8," Fed. Reg. 41(111), 23087-90 (1976).

A-8. Environmental Protection Agency, "Determination of Nitrogen Oxide Emissions From Stationary Sources, 40 CFR 60, App. A, Reference Method 7," Fed. Reg. 41(111), 23085-87 (1976).

A-9. Leichnity, J., Detector Tube Handbook, 2nd ed. Dragerwerk, A. G. Lubeck, October 1973.

A-10. Environmental Protection Agency, "Determination of Moisture in Stack Gases, 40 CFR 60, App. A, Reference Method 4," Fed. Reg. 41(111), 23072-76 (1976).

A-11. Weissburg, B. G., "Determination of Mercury in Soils by Flameless Atomic Absorption Spectrometry," Econ. Geol. 66(7), 1042 (1971).

A-12. Perry, John H., Chemical Engineers' Handbook, 5th ed. New York, NY, McGraw-Hill, 1973.

A-13. Code of Federal Regulations 40, Protection of the Environment, Pts. 60-99, Revised ed. Washington, DC, General Services Admin., Office of the Federal Register, July 1976.

A-14. American Society for Testing and Materials, 1973 Annual Book of ASTM Standards. Pt. 23, Water; Atmospheric Analysis. Philadelphia, PA, 1973.

A-15. American Society for Testing and Materials, "Standard Recommended Practice for Sampling Industrial Chemicals," E300-73, in ASTM Book of Standards 1973. Philadelphia, PA, 1973, P. 601.

A-16. Environmental Protection Agency, Office of Technology Transfer, Handbook for Monitoring Industrial Waste Water. August 1973.

A-17. Hamersma, J. W., S. L. Reynolds, and R. F. Maddalone, IERL-RTP Procedures Manual: Level 1 Environmental Assessment. EPA 600/2-76-106a. Redondo Beach, CA, TRW Systems Group, June 1976.

A-18. Hamersma, J. W., and S. L. Reynolds, Tentative Procedures for Sampling and Analysis of Coal Gasification Processes. Redondo Beach, CA, TRW Systems Group, March 1975.

A-19. Oldham, Ronald G., and Robert G. Wetherold, Assessment, Selection, and Development of Procedures for Determining the Environmental Acceptability of Synthetic Fuel Plants Based on Coal, Revised Report, 4 vols. FE-1795-3. Austin, TX, Radian Corp., May 1977.

A-20. Radian Corporation, Characterization of the Effluents From the CO_2 Acceptor Process, Sampling Plan. Tech. Note 200-154-04. Austin, TX, December 1976.

A-21. Harris, W. E., and Byron Kratochvii, "Sampling Variance In Analysis for Trace Components in Solids. Preparation of Reference Samples," Anal. Chem. 46(2), 313 (1974).

A-22. American Society for Testing and Materials, 1974 Annual Book of ATSM Standards. Pt. 26, Gaseous Fuels; Coal and Coke; Atmospheric Analysis. Philadelphia, PA, 1974.